

NUCLEAR RESONANCE OF O^{17} IN LIQUID
AND SOLID CARBON MONOXIDE

BY

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To my parents

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A study of molecular motions in various phases of carbon monoxide has been performed through nuclear magnetic resonance (NMR) spin-lattice relaxation time T_1 measurements in the liquid phase, T_1 and quadrupole perturbed NMR spectra in the β -phase and nuclear quadrupole resonance (NQR) linewidth and T_1 measurements in the α -phase in a sample enriched 24.5% with O^{17} .

The tumbling rotational motion in the liquid phase and its temperature dependence are obtained. An activation enthalpy of 198 ± 3 cal/mole is derived from the T_1 measurements. Information on features of the precessional motion about the crystal C axis in the β -phase is also obtained. The effective quadrupole coupling constants are compared with the static quadrupole coupling constant obtained in the NQR measurement of the α -phase. The former is shown to be three orders of magnitude smaller by precessional motion averaging. The temperature dependence of the effective quadrupole constant is also derived. It is shown that,

as the temperature increases, the average deviation of the precessional angles from the magic angle increase from $3.23 \pm 0.06^\circ$ at 61.9 K to $3.36 \pm 0.06^\circ$ near the triple point. T_1 measurements in the solid β -phase were also obtained.

In the α -phase the quadrupole interaction is sufficiently large enough to perform a pure quadrupole resonance experiment. The measurements in the α -phase provide the magnitude of the intramolecular quadrupole interaction. Furthermore, the NQR O^{17} linewidths exhibit a peculiar and unexpected behavior with a maximum around 37 K and a divergence for $T \leq 28$ K. The effective T_1 measurements in the temperature range from 49 ~ 55 K support the assumption that the linewidth is determined by the molecular motions in the α -phase. This behavior has been analyzed on the basis of a model of molecular reorientational processes. These processes could account for the residual entropy previously observed in the crystal. Comparison of the data with the theoretical picture allows one to derive information on the details of the molecular reorientations and their temperature dependence.

CHAPTER I INTRODUCTION

1. 1 Physical Properties of CO

Carbon monoxide is one of the most interesting diatomic molecular crystals and has been studied extensively [1-12]. Besides its structural simplicity and its similarity to other diatomic molecular crystals [6,9,13,14], CO exhibits some peculiar behavior which is probably related to the electric dipole-dipole interaction of the molecules [5,15]. Since the observation of residual entropy [4], interest has been focused on the possibility of an ordering transition. Gill and Morrison extended the studies to lower temperatures and found no transition occurring [10]. However, an anomaly in heat capacity near 18 K has been reported [16]. A theoretical calculation of the rate of ordering based on the model of a twofold barrier for end-over-end rotation in solid α -CO found the rate to be unobservably slow [17].

1. 1. 1 Crystal Structure of CO

There are two solid phases, α and β , of CO. At low temperatures, X-ray diffraction studies showed that the crystal structure of the α -phase is primitive cubic with a basis of four molecules per unit cell and that the molecules are aligned in the body diagonal directions as shown in Figure 1-1. However, two space groups $Pa\bar{3}$ (T_h^6) [18] and $P2_13$ (T^4) [1] are compatible with this arrangement. The $P2_13$ space group differs from $Pa\bar{3}$ in that each molecular center is displaced by a small amount δ along the direction of the molecular axis. The problem concerning which is the correct structure for α -CO is still in dispute [19].

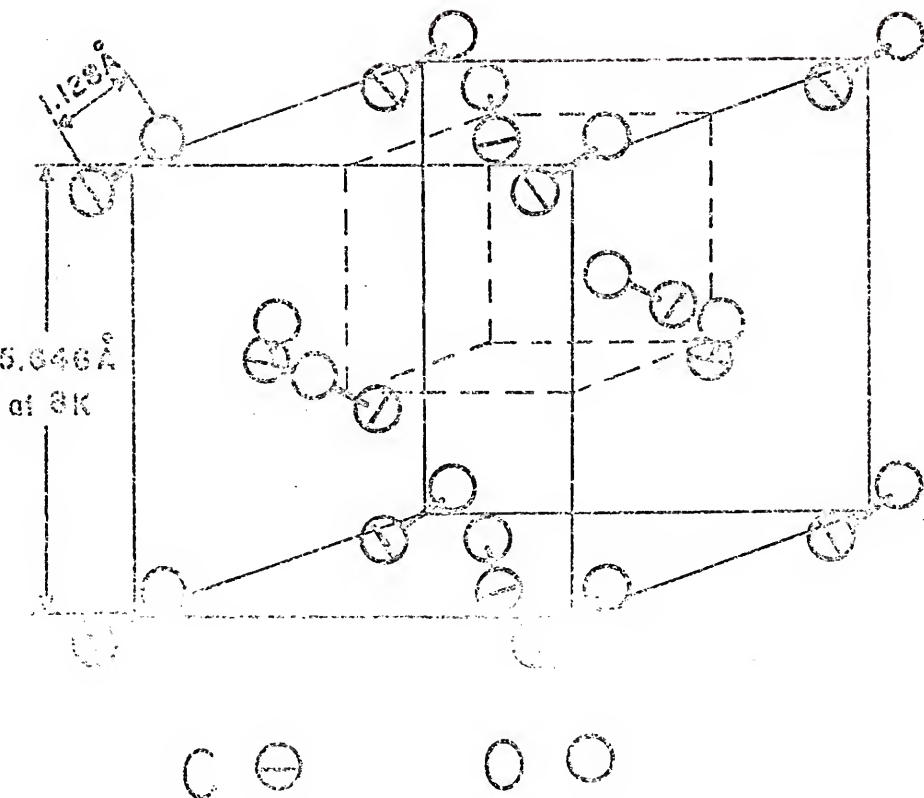


Figure 1-1. Crystal structure of α -CO. The molecules are aligned parallel to the body diagonals.

In the β -phase which occurs above 61.6 K, the crystal structure determined by Vegard [2] was that of β -N₂, and subsequent X-ray diffraction studies of β -N₂ [20] deduced this space group as $P6_3/mmc(D_6^{3h})$. In this regard one considers the crystal structure of β -CO, the same structure as β -N₂, to be hexagonal close packed. It was found that X-ray form factors were equally consistent with a dynamic model where the molecules precess about the C-axis at an angle θ' as shown in Figure 1-2, or with a static disordered model in which the molecules are randomly distributed among the 24 general positions of space group $P6_3/mmc$ [20].

1. 1. 2 Phase Diagram of CO

The phase diagram of CO has been determined by Fukushima, Gibson, and Scott up to a pressure of 1.75 Kbar using the change in nuclear spin-spin relaxation time T_2 of C¹³ as an indicator of the transition [21]. The phase diagram is shown in Figure 1-3. The α, β phase transition is at 61.6 K at equilibrium vapor pressure, and the triple point is at 68.15 K.

Applying the Clausius-Clapeyron equation, $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$, to the phase transition boundaries the volume increments at zero pressure are deduced to be $\Delta V_m = 2.50 \text{ cm}^3/\text{mole}$ and $\Delta V_{\alpha\beta} = 0.92 \text{ cm}^3/\text{mole}$ [21]. While the change of the volume in N₂ is $\Delta V_m = 2.5 \text{ cm}^3/\text{mole}$ [22], which is comparable to CO. However, $\Delta V_{\alpha\beta}$ in N₂ has a much smaller value, 0.31 cm³/mole [23,24].

The compression experiments found no new phase at higher pressures [25]. This is unlike N₂ where a new phase was found at higher pressures with a tetragonal structure [26].

1. 1. 3 Specific Heat and Other Thermodynamic Properties of CO

The heat capacity of CO has been measured [3,4,10] and is shown in Figure 1-4. The analysis of the results is compared with the entropy calculated from the band spectrum of CO in the gas phase. The discrepancy

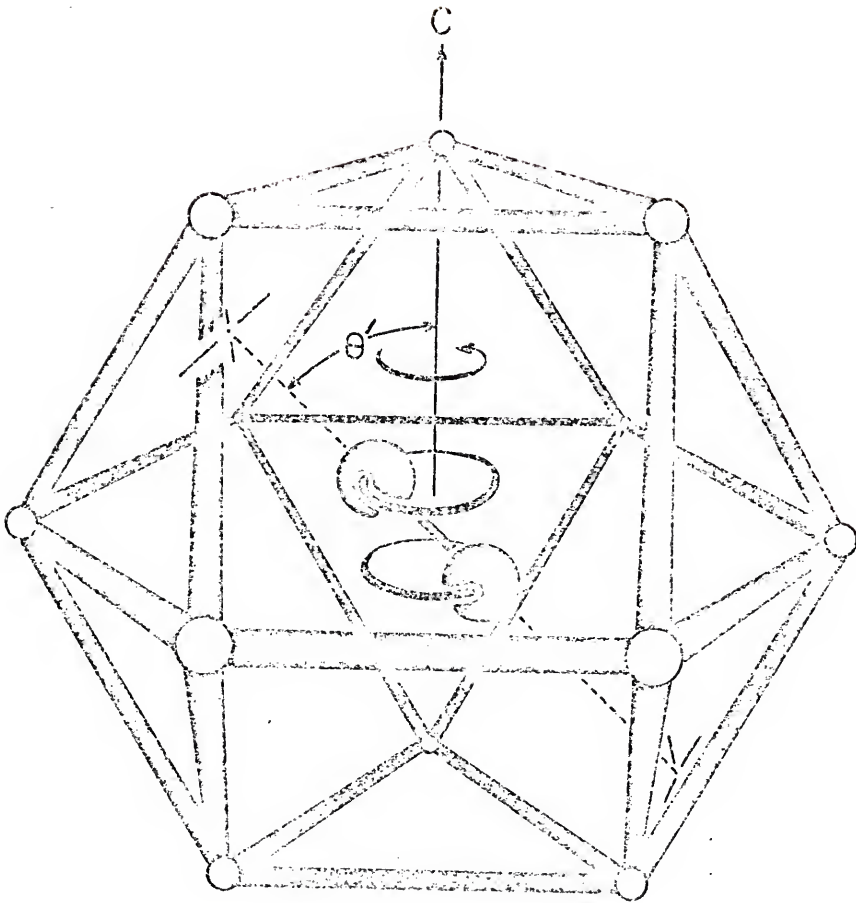


Figure 1-2. Crystal structure of β -CO. Open circles representing the cage structure denote hcp positions of molecules. Only the center molecule is illustrated which precesses around the crystal C axis with angle θ near the magic angle.

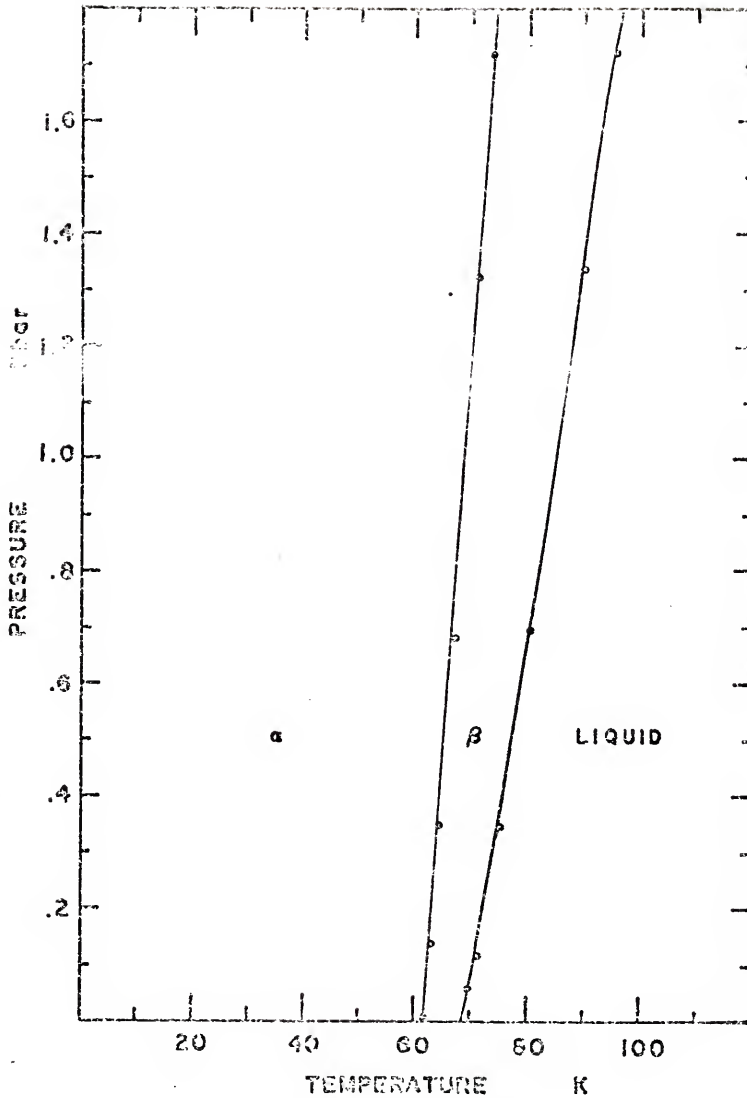


Figure 1-3. Phase diagram of CO in the P-T plane. The α - β transition temperature at equilibrium vapor pressure is 61.6 K. The triple point is at 68.15 K. (Data are from Ref. [21]).

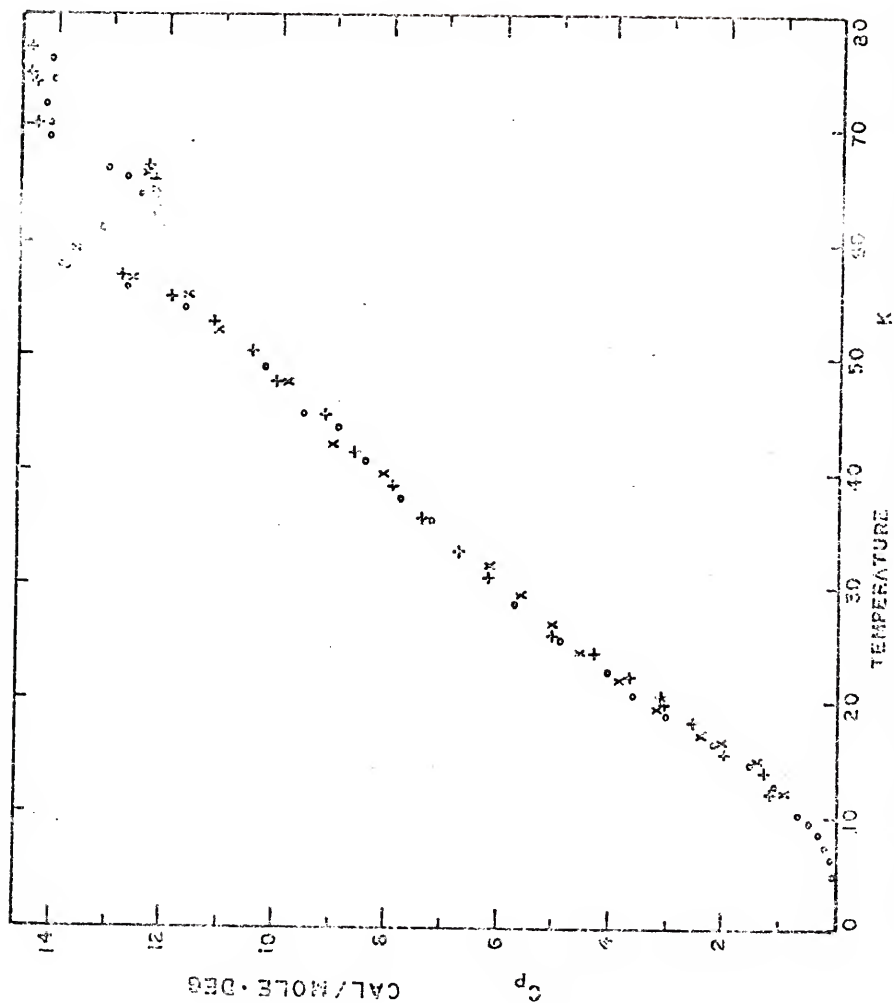


Figure 1-4. Heat capacity of CO. (The "+" data are from Clusius [3]. The "x" from Clayton and Giauque [4], and "o" from Gill and Morrison [10].)

was found to be approximately equal to $R \ln 2$. This was described as frozen in end-for-end disorder [4]. Melhuish and Scott [15] calculated the energy for the oriented and disoriented lattice and estimated the Curie temperature for the order-disorder transition. They found T_c to be ~ 5 K for CO. However, heat capacity measurements on solid α -CO have been carried to 2.5 K by Gill and Morrison with no indication of the occurrence of the transition [10]. The adiabatic compressibility χ_s may be calculated from the sound velocities and density using the equation

$$\chi_s = [\rho (V_l^2 - \frac{3}{4}V_t^2)]^{-1} \quad (1-1)$$

where V_l and V_t are the longitudinal and transverse sound velocities, and ρ is the density.

Voitovich et al. [27] measured V_l and V_t and thereby χ_s was obtained. While from the thermodynamic equations one has

$$\chi_T = \chi_s + \beta^2 TV/C_p \quad (1-2)$$

and

$$\chi_T/\chi_s = C_p/C_V \quad (1-3)$$

where χ_T is the isothermal compressibility, β is the thermal expansion, V is the molar volume and C_p and C_V are the specific heats at constant pressure and volume respectively. Krupsii et al. measured the thermal expansion of α -CO and applied the above equations using χ_s from [27] and C_p from [4,10] to give a complete table for lattice parameters, molar volume, volume expansion, specific heat at constant volume, and isothermal compressibility [18].

1. 2 Nuclear Magnetic Resonance

Consider an isolated nucleus in a steady magnetic field $\vec{H}_0$ and suppose that the nuclear spin number I is greater than zero, so that the nucleus possesses a magnetic moment. Quantum mechanically the angular momentum of the nucleus is quantized along the applied field direction with the magnetic number m taking values of $I, I-1, \dots, -(I-1), -I$. The Hamiltonian can be written as

$$H = -\vec{\mu} \cdot \vec{H}_0 \quad (1-4)$$

where μ is the nuclear magnetic moment and H_0 is an externally applied field. The magnetic moment is related to the nuclear spin angular momentum by

$$\gamma \hbar \vec{I} = \vec{\mu} \quad (1-5)$$

where γ is the gyromagnetic ratio of the nucleus, $\hbar$ equals $\frac{h}{2\pi}$ where h is Planck's constant. The components of the magnetic moment are thus given by the $(2I+1)$ value of μ , $\mu(I-1)/I, \dots, -\mu(I-1)/I, -\mu$. The energy levels of the nuclear magnet in the magnetic field $\vec{H}_0$ are therefore equally spaced taking values of $m\mu H_0/I$, where $m = I, (I-1), \dots, -(I-1), -I$. From the classical point of view the nucleus may be regarded as a magnet dipole $\vec{\mu}$ precessing about the direction of the applied field $\vec{H}_0$. The rate of precession is given by the well known Larmor angular frequency

$$\omega_L = \gamma H_0 \quad (1-6)$$

If an additional small magnetic field $\vec{H}_1$ is applied at right angles to $\vec{H}_0$, the dipole $\vec{\mu}$ will experience a torque of $\vec{\mu} \times \vec{H}_1$ tending to increase the angle θ between $\vec{\mu}$ and $\vec{H}_0$. If $\vec{H}_1$ is made to rotate about $\vec{H}_0$ as axis, with

the same frequency as the Larmor frequency ω_L , then the angle θ will steadily increase. For rotation frequencies differing from ω_0 the coupling between $\vec{I}$ and $\vec{H}_1$ will merely produce small perturbation of the precessional motion with no net affect [28]. Hence the application of a radio frequency field $\vec{H}_1$ at a frequency ω_L will cause energy to be absorbed by the nucleus. The experimental spectrum will be an infinite sharp line at the Larmor frequency ω_L . However, the effect of the neighboring nuclei will produce a local magnetic field at each nuclear site. This will cause the line to be broadened. However, this broadening is also effected by the distances and relative directions between the neighboring nuclei as well as their motions. Nuclear Magnetic Resonance (NMR) measurements thus provide useful information about the molecular structure and the molecular dynamics in the solid and liquid phases. For example, in a single crystal from the linewidth in the solid, it is possible to calculate the second moment M_2 . Thus one will have the information about the separations and directions between nuclei in a unit cell. While for a powder sample it is not possible to determine the directional relation between nuclei, it is still possible to find out their separations. Moreover, a dramatic change of M_2 may indicate the onset of the rotation of the molecules in the solid and further reduction of linewidth could be a clue to the diffusion of the molecules in the solid. Other examples include chemical shifts in the liquid phase for identification and analysis of the substance, Knight shifts for studying information about the conducting electrons near the Fermi surface, observation of chemical reactions processes from the growth of the signal strength [28], and finally the molecular motions through the spin-lattice relation time T_1 measurements as one will see later in this experimental study of CO.

1. 3 Nuclear Quadrupole Resonance

The interaction of a charge distribution with an electrical potential due to the external sources is given by

$$E = \int \rho(\vec{r}) V(\vec{r}) d^3r \quad (1-7)$$

where $V(r)$ is the electrostatic potential. Regarding the nucleus as a charge distribution, and expanding $V(r)$ about the origin of the center of mass of the nucleus, one obtains

$$E = V(0) \int \rho(\vec{r}) d^3r + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho(\vec{r}) d^3r + \frac{1}{2} \sum_{\alpha\beta} V_{\alpha\beta} \int x_{\alpha} x_{\beta} \rho(\vec{r}) d^3r \quad (1-8)$$

where x_{α} , $\alpha = 1, 2, 3$, stands for x, y, z , respectively and

$$V_{\alpha} = \frac{\partial V}{\partial x_{\alpha}} \Big|_{\vec{r}=0}, \quad V_{\alpha\beta} = \frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \Big|_{\vec{r}=0}.$$

The first term on the right hand side of (1-8) is the electrostatic energy of the nucleus taking the nucleus as a point charge. The second term involves the electric dipole moment of the nucleus. Since the wave function of the nucleus has definite parity, $\rho(\vec{r}) = \rho(-\vec{r})$, the electric dipole moment of the nucleus vanishes [29]. One is only interested in the third term, the electric quadrupole interaction now. By introducing

$$Q_{\alpha\beta} = \int (3x_{\alpha} x_{\beta} - \delta_{\alpha\beta} r^2) \rho(\vec{r}) d^3r$$

and using the fact that

$$\sum_{\alpha} \frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\alpha}} = 0,$$

one has for the quadrupole term

$$E_Q = \frac{1}{6} \sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta} \quad (1-9)$$

In quantum mechanics, one considers ρ as an operator

$$\rho^{(op)}(\vec{r}) = e \sum_{K=\text{protons}} \rho(\vec{r} - \vec{r}_K) \quad (1-10)$$

and defines the operator $Q_{\alpha\beta}^{(op)}$ as

$$\begin{aligned} Q_{\alpha\beta}^{(op)} &= \int (3x_\alpha x_\beta - \delta_{\alpha\beta} r^2) \rho^{(op)}(\vec{r}) d^3 r \\ &= e \sum_{K=\text{protons}} (3x_{\alpha K} x_{\beta K} - \delta_{\alpha\beta} r_K^2) \end{aligned} \quad (1-11)$$

From (1-9) one writes the Hamiltonian

$$H_Q = \frac{1}{6a_B} \sum_{\alpha, \beta} V_{\alpha\beta} Q_{\alpha\beta}^{(op)} \quad (1-12)$$

The Wigner-Eckart theorem states that the set of matrix elements of an irreducible tensor operator A^2 differs from any other irreducible tensor B^2 only by a constant factor [30]. The tensor operator $Q_{\alpha\beta}^{(op)}$ then is related to the tensor operator $Q(I)$ as

$$\begin{aligned} Q_{\alpha\beta}^{(op)} &= e \sum_{K=\text{protons}} (3x_{\alpha K} x_{\beta K} - \delta_{\alpha\beta} r^2) \\ &= CQ(I) \\ &= C \left(3 \frac{I_\alpha I_\beta + I_\beta I_\alpha}{2} - \delta_{\alpha\beta} I^2 \right) \end{aligned} \quad (1-13)$$

Since $Q_{\alpha\beta}^{(op)}$ can be written as combinations of irreducible tensors like $Q(I)$. Defining eQ , quadropole moment of nucleus, as

$$eQ = \langle I, I | e \sum_{K=\text{protons}} (3z_K^2 - r_K^2) | I, I \rangle \quad (1-14)$$

and operating on the matrix element nm' in (1-13) for $m = I$, $m' = I$ where I is the nuclear spin, it follows that

$$C = \frac{eQ}{I(2I-1)} \quad (1-15)$$

In order for C to have a physical meaning it follows that one needs $I > \frac{1}{2}$ to have a quadrupole interaction. From (1-12), (1-13), and (1-15) it follows that

$$H_Q = \frac{eQ}{6I(2I-1)} \sum_{\alpha, \beta} V_{\alpha\beta} \left[\frac{3}{2} (I_\alpha I_\beta + I_\beta I_\alpha) - \delta_{\alpha\beta} I^2 \right] \quad (1-16)$$

In the principal axes of the field gradient, one defines $eQ = V_{ZZ}$ and the asymmetry parameter

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

where V_{XX} , V_{YY} , and V_{ZZ} are the principal field gradients. One then has from (1-16)

$$H_Q = \frac{e^2 Q q}{4I(2I-1)} [3I_Z^2 - I^2 + \eta (I_X^2 - I_Y^2)] \quad (1-17)$$

One can also write (1-16) in the laboratory frame as

$$H_Q = \frac{eQ}{4I(2I-1)} \left[\frac{\sqrt{6}}{3} V_0 (3I_Z^2 - I^2) + V_+ (I_- I_Z + I_Z I_-) + V_- (I_+ I_Z + I_Z I_+) + V_{+2} (I_-)^2 + V_{-2} (I_+)^2 \right] \quad (1-18)$$

where

$$\begin{aligned} V_0 &= \frac{3}{\sqrt{6}} V_{ZZ} \\ V_{\pm 1} &= V_{XZ} \pm i V_{YZ} \\ V_{\pm 2} &= \frac{i}{2} (V_{ZZ} - V_{YY}) \pm i V_{XY} \end{aligned}$$

and $I_+ = I_X + iI_Y$, $I_- = I_X - iI_Y$ are the raising and lowering angular momentum operators respectively.

The quadrupole interaction is therefore due to the interaction of the nuclear quadrupole moment and the electric field gradient produced at the nuclear site by the external electric sources. Intermolecular electric

sources usually provide only a small amount compared with those of intramolecular origin. Nuclear quadrupole resonance (NQR) therefore provides a sensitive method to study the molecular motions as well as the electronic structure of the molecules. Comparison of the quadrupole coupling constant (QCC) of the free molecule obtained from microwave studies and that from NQR measurements in the solid phase provides information about the alteration of the electronic distribution in the solid state. NQR can also be used to study crystal structures, phase transitions, and impurity effects [31]. Nuclear quadrupole interactions usually provide a very effective mechanism for spin-lattice relaxation in the liquid phase. Thus it permits a direct determination of certain correlation times characterizing the molecular dynamics. The study of the linewidth and resonance frequency also elucidates the molecular motions in the solid phase.

CHAPTER II EXPERIMENTAL PROCEDURE

2. 1 The Sample

The predominant naturally occurring isotopes of carbon and oxygen do not possess nuclear moments. Therefore an NMR study of CO has to resort to enriched isotopes. C^{13} provides one of the possibilities [21,32,33]. For a comprehensive study of spin-lattice relaxation and quadrupole resonance in the low temperature phase of CO, O^{17} is the best choice. O^{17} with nuclear spin $I = \frac{5}{2}$ [34] has a nuclear quadrupole moment which, interacting with the molecular electric environment, provides the dominant mechanism of spin-lattice relaxation. From nuclear quadrupole resonance experiments which can only be performed with nuclear spin $I \geq 1$, the quadrupole coupling constant of O^{17} in CO can be deduced. Therefore a great deal of information about the CO molecules can be learned.

One liter of gaseous CO enriched to 24.5% in O^{17} was purchased from Prochem U. S. Service, Inc., New Jersey. The sample was claimed to have 99.9 atom % of C^{12} .

2. 2 The Cryostat and Temperature Measurements

The construction of the cryostat is shown in Figure 2-1. The condensed sample was held in a Kel-F cavity of 0.43 inch in diameter and 0.78 inch long. Surrounding the sample chamber was an rf coil wound from 30 turns of equally spaced #26 cotton covered copper wire. The inductance of the sample coil was approximately 10 μH which was used for NMR measurements operating at 4.098 MHz. Another sample coil made of ~100

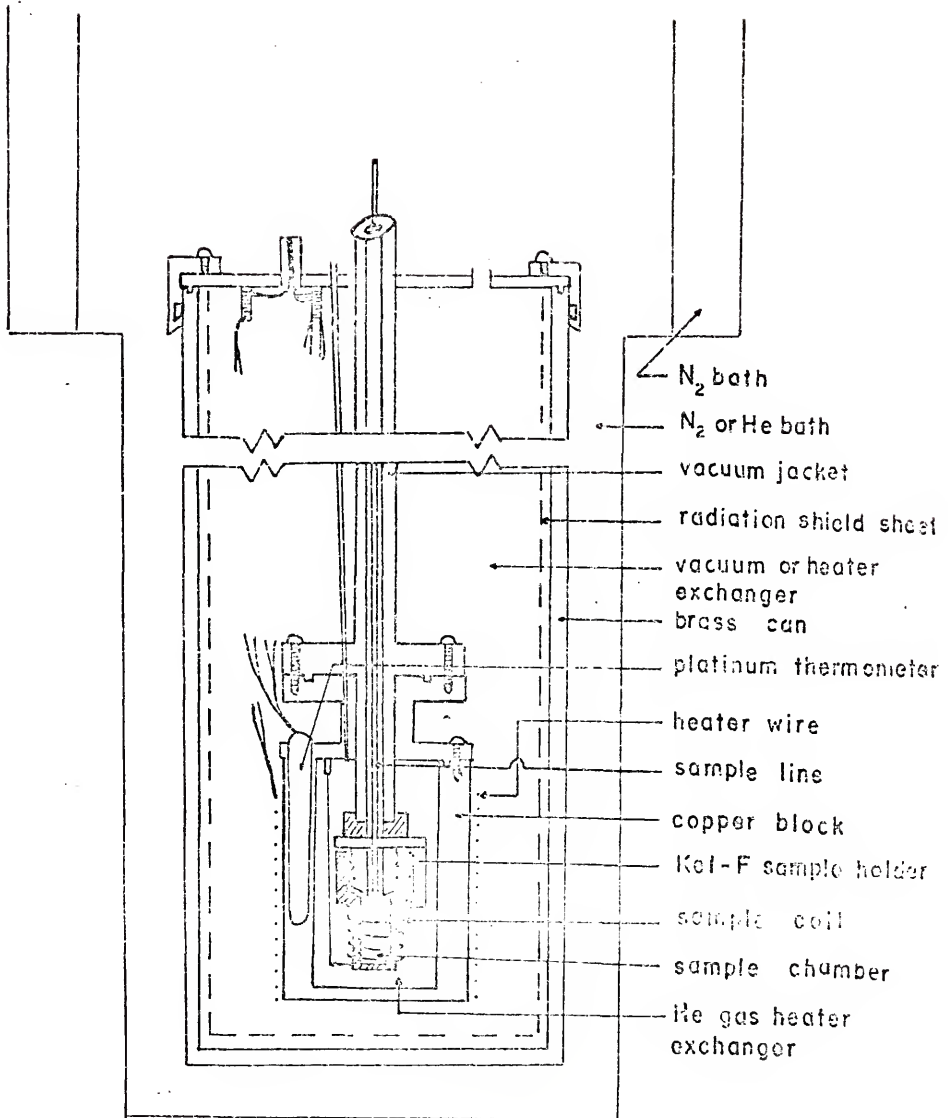


Figure 2-1. Sample cell and temperature-controlled cryostat.

turns of #36 enamel coated copper wire with an inductance of $\sim 100 \mu\text{H}$ was used in the NQR measurements at $\sim 1.1 \text{ MHz}$. The sample coil was connected to the spectrometer through the small stainless steel sample line. He gas was admitted into the copper block on which a platinum resistance thermometer was mounted. The He gas served as a heat exchanger between the sample and the copper block. The platinum thermometer calibrated by the National Bureau of Standards was used for two purposes. First, the conventional temperature measurement was achieved by connecting four leads to a Leeds and Northrup Mueller bridge. Secondly, the output of the galvanometer was phase shifted 180° then fed back to the power supply which controlled the current to the heater. With the Mueller bridge the temperature can be measured accurately to 0.01° K ; however, this experiment, due to the uncertainty in the different readings of the M and R mode in the Mueller bridge (because of using feed-back temperature control) a 0.05° K uncertainty should be assigned. Between the brass can and copper block, He gas could be introduced to serve as a heat exchanger in case temperature equilibrium of the sample with the liquid N_2 or liquid He was desired. To achieve a sample temperature higher than the surrounding bath, this space was evacuated to 10^{-4} torr or less. A thin brass sheet radiation shield held in place with small Kel-F pieces reduced additional radiation heat loss. Temperatures between 50 K and 77 K were achieved by pumping the N_2 bath and above 77 K the heater was applied. For temperatures below 50 K , liquid He was used as a cold bath with the heater on to maintain the desired temperature. Before the sample was introduced to the sample chamber, this space had been evacuated to 4×10^{-6} torr. To avoid solidified sample blocking the line before it reached to the sample chamber, a vacuum jacket was situated around the sample line.

2. 3 The Electromagnet

The electromagnet used in the NMR measurements was a Varian 4012-3B rotatable electromagnet with a 12 inch diameter pole face and a 3.5 inch gap. The magnetic field was regulated by a fieldial regulated system which utilized a Hall effect probe inside the magnetic field. The maximum magnetic field produced was around 9 KG. Taking long time stability and maximum sensitivity of the NMR signals into consideration, a 7.1 KG field strength seemed to be the best choice. This in turn produced a 4.098 MHz ^{17}O NMR signal in liquid CO. The rotation angle of the magnet could be adjusted to within 1° of accuracy. The inhomogeneity of the magnetic field over the sample volume was determined in the liquid phase to be ~ 0.1 gauss which gave a T_2^* of about 3.5 ms. After long hours of operation (~ 6 hrs.) the fluctuation of the magnetic field was found to be 3×10^{-4} /hr. or less.

2. 4 The Spectrometer

The pulse spectrometer used in this experiment is depicted in Figure 2-2. This set-up was used for the NMR experiments as well as the NQR measurements with only a few modifications of the receiver pre-amplifier. The high stability General Radio 1061 frequency synthesizer was the main rf source. Since it is a heterodyne system, the frequency was set to 10 MHz higher than the resonance frequency to utilize a 10 MHz amplifier and a phase sensitive detector. This signal when mixed with the gated 10 MHz reference frequency was amplified to approximately 2V peak to peak rf, before it entered the transmitter. The transmitter is adequate to supply high power pulsed output and low power continuous output. The magnetic field produced by the rf pulse was calculated to be ~ 30 gauss, which is large compared with the linewidths of the spectra being

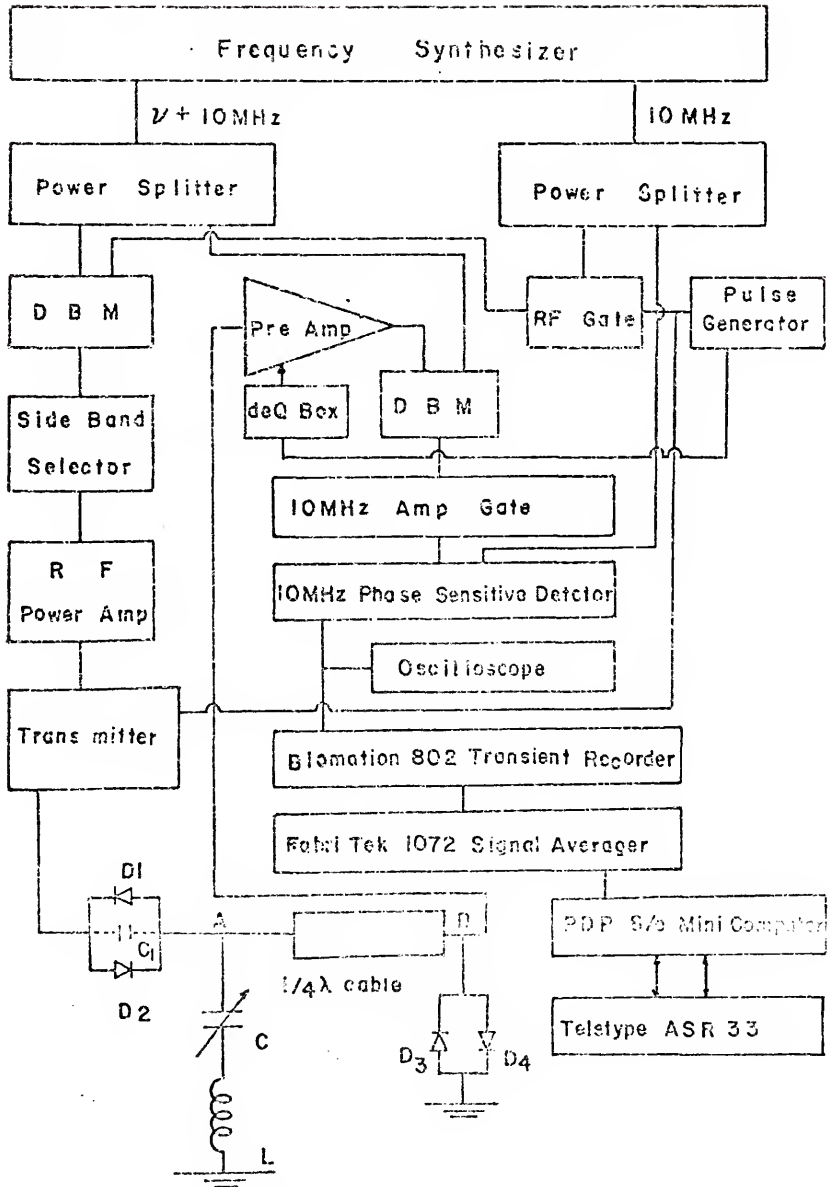


Figure 2-2. Block diagram of the pulsed NMR/NQR spectrometer.

studied. The same pulse which gated the 10 MHz frequency controlled and gated the final stage transmitter also.

In a pulse nuclear resonance experiment, the induction signal is typically obscured for several microseconds after the transmitter pulse by the ringing of the input tuned circuit. This ringing can be reduced by a weak coupling to the nonlinear input [35]. In this experiment, a photo-FET Q switch similar to the one described by Conradi [36] was used. During the time the high power rf pulse was on, the D_1D_2 cross-diode set conducted strongly. The D_3D_4 diode-set was also conducting to protect the receiver preamplifier and the photo-FET Q switch. When the cross-diode set D_3D_4 is conducting, point A of the $\frac{1}{4} \lambda$ cable appears as a high impedance. While the transmitter pulse is off, D_3D_4 ceases to conduct and point B is a high impedance.

When the rf level reaches 0.5 volt, the cross-diodes D_1D_2 turn off. This isolates the transmitter from the L. C. tuned circuit. Unfortunately, in practice the L. C. tuned circuit and the transmitter are still weakly coupled by the capacitor C_1 across diodes D_1D_2 . This coupling ties the voltage across the sample coil to the slow ringing down of the transmitter final stage [37], so the recovery time is prolonged. The negative bias FET was adjusted just into the cut-off region. A pulse from the pulse generator turned on a LED diode which provides light to turn on the Q switch. The source-drain path appears as a low resistance ($\sim 200\Omega$) which provides a low impedance path to ground for the energy of the ringing. The Q value of the input circuit hence was reduced during the time the Q quenching pulse was on, causing it to ring down quicker. Just as the ringing decreases to the order of the free induction signal ($\sim mV$), the Q quenching pulse was turned off to restore a high Q value

in the receiver preamplifier for detecting the free induction signal. The amplified signal was then mixed with the rf frequency ($\nu + 10$ MHz) split from the same source. The combined signal was then phase sensitive detected by mixing with the 10 MHz reference signal.

The output signal was observed on an oscilloscope and also fed to the Biomation 802 transient recorder which captured the fast signal for slower transfer to the Fabri-Tek 1072 signal averager. A PDP 8/E mini-computer was interfaced with the Fabri-Tek 1072 to perform the Fourier transformation of the signal from the time domain (free induction decay) into the frequency domain (spectrum). The result was then plotted on an X-Y recorder.

CHAPTER III LIQUID PHASE

3. 1 NMR Spin-Lattice Relaxation

In the liquid phase, due to the fast molecular tumbling motions, the quadrupole interaction is averaged to zero. The experimental NMR signal will, therefore, be a single line. The linewidths are mainly the result of the inhomogeneity of the applied magnetic field. The random motions of the molecules also provide the mechanisms for the nuclear spin system to relax when perturbed from its equilibrium state. T_1 measurements thus can be used to study the molecular motions. In the liquid, the energy differences between the Zeeman levels are all equal. The fast spin-exchange mechanism thus maintains a Boltzmann distribution of the nuclear populations among the energy levels [38], i.e. a spin temperature can be defined and the relaxation to the lattice temperature is governed by a single exponential decay. In order to describe the macroscopic relaxation time T_1 through the microscopic molecular motions, one considers the time dependent Hamiltonian $H_1(t)$ caused by the molecular motions. This $H_1(t)$ represents a small perturbation and induces transitions between eigenstates of the Zeeman Hamiltonian. The correlation function of $H_1(t)$ is then introduced which expresses a correlation between the two different configurations of a nuclear environment at two different times. The rate equations among the energy levels are then considered. This connects the relations between the experimental relaxation of the total magnetization and the correlation time of the tumbling motions of molecules.

Consider $H_1(t)$ a small perturbation among the eigenstates $|\alpha\rangle, \dots, |\beta\rangle$, etc. with eigenenergies α, β etc. of a spin system S . The transition probability per unit time for a transition from state $|\beta\rangle$ to state $|\alpha\rangle$, assuming the system S at time zero is in state $|\beta\rangle$, time dependent perturbation theory gives [6]

$$W_{\alpha\beta} = \frac{1}{\hbar^2} \int_0^t \langle \beta | H_1(t) | \alpha \rangle \langle \alpha | H_1(t') | \beta \rangle e^{i\omega_{\alpha\beta}(t'-t)} dt + \text{C. C.} \quad (3-1)$$

where $W_{\alpha\beta} = \frac{\alpha - \beta}{\hbar}$. Taking the average $\bar{W}_{\alpha\beta}$ over a statistical ensemble, and introducing the correlation function $G_{\alpha\beta}$ as

$$G_{\alpha\beta}(t-t') = \overline{\langle \beta | H_1(t) | \alpha \rangle \langle \alpha | H_1(t') | \beta \rangle} \quad (3-2)$$

One uses the properties that the random function $\langle \alpha | H_1(t) | \beta \rangle$ is stationary, i.e. $G_{\alpha\beta}$ depends on t and t' only through the difference $t - t' = \tau$. It follows that

$$\begin{aligned} \bar{W}_{\alpha\beta} &= \frac{1}{\hbar^2} \int_0^t G_{\alpha\beta}(\tau) e^{-i\omega_{\alpha\beta}\tau} d\tau + \text{C. C.} \\ &= \frac{1}{\hbar^2} \int_{-t}^t G_{\alpha\beta}(\tau) e^{-i\omega_{\alpha\beta}\tau} d\tau \end{aligned} \quad (3-3)$$

Since one usually considers a time $t \gg \frac{1}{\omega_{\alpha\beta}}$, it turns out that the limits of the integration in (3-3) can be replaced by $\pm \infty$ and one has

$$\bar{W}_{\alpha\beta} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} G_{\alpha\beta}(\tau) e^{-i\omega_{\alpha\beta}\tau} d\tau \quad (3-4)$$

In most cases $H_1(t)$ can be expressed as a combination of two irreducible tensors of rank k . Let

$$H_1(t) = \sum_{p=-k}^k A^{(p)}(t) B^{(p)}(t) \quad (3-5)$$

where A is the spin part of the Hamiltonian and B is that part of the spatial coordinates which is time dependent. It follows that (3-4) can be written as

$$\bar{W}_{\alpha\beta} = \sum_{p=-k}^k \frac{1}{h^2} \left| \left\langle \alpha | A^{(p)} | \beta \right\rangle \right|^2 g^{(p)}(\tau) e^{-i\omega_{\alpha\beta}\tau} d\tau \quad (3-6)$$

where

$$g^{(p)}(\tau) = \overline{B^{(p)}(t) B^{*(p)}(t-\tau)}$$

is the correlation function of $B^{(p)}(t)$.

There are various possible mechanisms of relaxation, (1) the intramolecular quadrupole interaction, (2) the intramolecular spin-rotation interaction, (3) the intramolecular anisotropic chemical shift interaction, (4) the intermolecular magnetic dipole-dipole interaction and (5) the intermolecular electric quadrupole-dipole interaction. However, an estimate of the magnitudes shows that the spin-lattice relaxation is almost completely dominated by the intramolecular quadrupole interaction.

3. 2 Intramolecular Relaxation Mechanisms

The interaction between the nuclear moments and the electrons in the CO molecule drives the transition among the Zeeman levels of O^{17} nuclei. In principle there are three relaxation mechanisms which are of intramolecular origin. They are (1) the intramolecular quadrupole interaction, (2) the spin rotation interaction and (3) the anisotropic chemical shift interaction.

Consider (1) the intramolecular quadrupole interaction. In Appendix A it is shown that

$$\frac{1}{T_1} = \frac{3}{125} \left(\frac{e^2 Q q}{h} \right)^2 \tau_2 \quad (3-7)$$

where $\frac{e^2 Qq}{h}$ is the static quadrupole coupling constant, which one has determined in the NQR measurement of CO in the α -phase to be 4.20 MHz and τ_2 is the autocorrelation time of the molecular tumbling motions. If one adopts the value of τ_2 from Raman anisotropic scattering [39] to be $\tau_2 = 3 \times 10^{-13}$ sec. at a temperature of 77 K one has $\frac{1}{T_1} = 4.17 \text{ sec}^{-1}$ while the experimental T_1 at 77 K is 220 ms. This gives $\frac{1}{T_1} = 4.54 \text{ sec}^{-1}$.

In (2) the spin-rotation interaction, the time fluctuation of the interactions of the nuclear spins with the angular momentum of the molecule provides a relaxation mechanism for the nuclear spins. Assuming a Langevin equation for the angular momentum and a rotational diffusion of Debye type, Hubbard obtained [40]

$$\left(\frac{1}{T_1}\right)_{\text{s.r.}} = \frac{(2C_{\perp} + C_{\parallel})^2}{9\hbar^2} 2IKT\tau_J + \frac{2(C_{\parallel} - C_{\perp})^2}{9\hbar^2} 2IKT \left(\frac{1}{\tau_J} + \frac{1}{\tau_2}\right)^{-1} \quad (3-8)$$

where $C_{\perp}$ and $C_{\parallel}$ are the components of the spin-rotation tensor perpendicular and parallel to the axis directed from the center of mass of the molecule to the resonant nucleus. I is the moment of inertia about a line through the center of mass and perpendicular to the molecular axis. I is related to the angular momentum of the molecule $\vec{J}$ by $I\vec{\omega} = \hbar\vec{J}$. τ_J is the correlation time for the angular momentum of the molecule and τ_2 is the correlation time for molecular reorientation.

Liquids near their melting points are often described by a reorientation process called the "diffusion limit" in which the molecules turn through a very small angle between collisions and τ_2 and τ_J are related by the following equation [41]:

$$\tau_J \tau_2 = \frac{I}{6KT} \quad (3-9)$$

For linear molecules one has $3 C_{\text{eff}}^2 = 2 C_{\parallel}^2 + C_{\perp}^2 = 2 C_{\perp}^2$. Assuming the diffusion limit for the temperature of interest one has from (3-8) and (3-9)

$$\left(\frac{1}{T_1} \right)_{\text{s.r.}} = \frac{C_{\text{eff}}^2}{3\hbar^2} \frac{1}{\tau_2} \quad (3-10)$$

Using the value $C_{\text{eff}} = 23.1 \text{ KHz}$ [42] and τ_2 from Raman experiments [39] one finds $\left(\frac{1}{T_1} \right)_{\text{s.r.}} = 3.6 \times 10^{-5} \text{ sec}^{-1}$ which is negligibly small compared with (3-7).

Consider (3) the anisotropic chemical shift. The interactions of the external D.C. magnetic field with the electrons around the resonant nucleus in a molecule produces a magnetic field at the nuclear site. The anisotropy of this coupling under the molecular motions may introduce transitions between energy levels. In the fast motion regime one has [43]

$$\left(\frac{1}{T_1} \right)_{\text{a.c.}} = \frac{2}{15} \gamma^2 H_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_2 \quad (3-11)$$

where γ is the gyromagnetic ratio of nucleus ^{17}O . H_0 is the applied D.C. magnetic field. $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the parallel and perpendicular parts of the chemical shift tensor in the principal reference frame respectively. τ_2 is the correlation time for molecular tumbling motions described before.

Using the value cited by Appleman and Dailey [44] that $(\sigma_{\parallel} - \sigma_{\perp})$ for the ^{17}O nucleus in CO is 4.6×10^{-6} and 7.1 KG for the external magnetic field H_0 one calculates

$$\left(\frac{1}{T_1} \right)_{\text{a.c.}} = 5.6 \times 10^{-6} \text{ sec}^{-1}.$$

One notes from the small value that the relaxation due to the anisotropic chemical shift interaction can be neglected. By neglecting the spin-rotation and the anisotropic chemical shift the calculated value of

4.17 sec^{-1} for the intramolecular quadrupole interaction is in good agreement with the experimental value of 4.54 sec^{-1} .

3. 3 Intermolecular Relaxation Mechanisms

The spin-lattice relaxation may also arise from the interactions of the O^{17} nuclei with the intermolecular fields. There are two mechanisms which, in principle, could induce transitions in the absence of a rf field. They are (1) the intermolecular magnetic dipole-dipole interaction and (2) the intermolecular electric quadrupole-dipole interaction.

Consider first (1) the magnetic dipole-dipole interaction. Following Bloembergen, Purcell and Pound [45] by assuming spherical molecules and a Debye model of diffusion, one would have a $\frac{1}{T_1}$ contribution from intermolecular magnetic dipole-dipole interaction given by the following equation:

$$\left(\frac{1}{T}\right)_{i.d.} = \frac{3\pi}{10} \frac{\gamma^4 \hbar^2 N_0}{aD} \quad (3-12)$$

where $2a$ is the closest approach of the neighboring molecules, D is the diffusion coefficient of the liquid and N_0 is the number of molecules per cm^3 . Using D as $2.9 \times 10^{-5} \text{ cm}^2/\text{sec}$ [46] and the density of liquid CO as 0.803 g/cm^3 , which gives $N_0 \approx 1.72 \times 10^{22}/\text{cm}^3$ and $2a \approx 3.87 \times 10^{-8} \text{ cm}$, one obtains

$$\left(\frac{1}{T}\right)_{i.d.} \approx 4.5 \times 10^{-6} \text{ sec}^{-1}.$$

Now consider (2) the intermolecular electric quadrupole-dipole interaction. It is well known that the CO molecule possesses a dipole moment of $0.11 \times 10^{-18} \text{ esu}$ [5]. The electric dipoles of neighboring CO molecules thus produce a field gradient at the O^{17} nucleus site. This is similar to the intramolecular quadrupole interaction except now the field gradient

is due to remote electric sources. Assuming again a Debye type diffusion for the liquid following the calculations of Bonera and Rigamonti [47], one has

$$\left(\frac{1}{T_1}\right)_{i.q.} = \frac{9\pi}{10} \frac{e^2 Q^2 M^2 N_0}{\hbar^2 D a^3} \quad (3-13)$$

where a , N_0 , and D have the same definitions as discussed in the magnetic dipole-dipole interaction. eQ is the quadrupole moment of nucleus O^{17} , and M is the dipole moment of the CO molecule. Taking the value of Q measured by Stevenson and Townes [48] as $-0.026 \times 10^{-24} \text{ cm}^3$, one calculates

$$\left(\frac{1}{T_1}\right)_{i.q.} \approx 4.4 \times 10^{-4} \text{ sec}^{-1}.$$

From the above considerations one immediately concludes that the spin-lattice relaxation in liquid CO is completely dominated by the intramolecular quadrupole interaction. This is usually true for NMR spin-lattice relaxation of most substances possessing a nuclear quadrupole moment in the liquid phase.

3. 4 Temperature Dependence of Spin-Lattice Relaxation Time

Using the conventional $\frac{\pi}{2} - \tau - \frac{\pi}{2}$ pulse sequence, one measures the spin-lattice relaxation time T_1 in the liquid phase. Figure 3-1 shows the experimental T_1 values at different temperatures. Data were taken during a period of several months. Due to the uncertainty in the T_1 measurements, a 10% error should be assigned to each point. In view of the cluster of points taken at different times, it shows no impurity is effectively absorbed in the sample during the course of experiments.

By assuming the intramolecular quadrupole interaction is the only contribution to T_1 and using the NQR measurements extrapolated to zero temperature, one would have $\frac{e^2 Q q}{h} \approx 4.20 \text{ MHz}$. From this one has the following relation for liquid CO

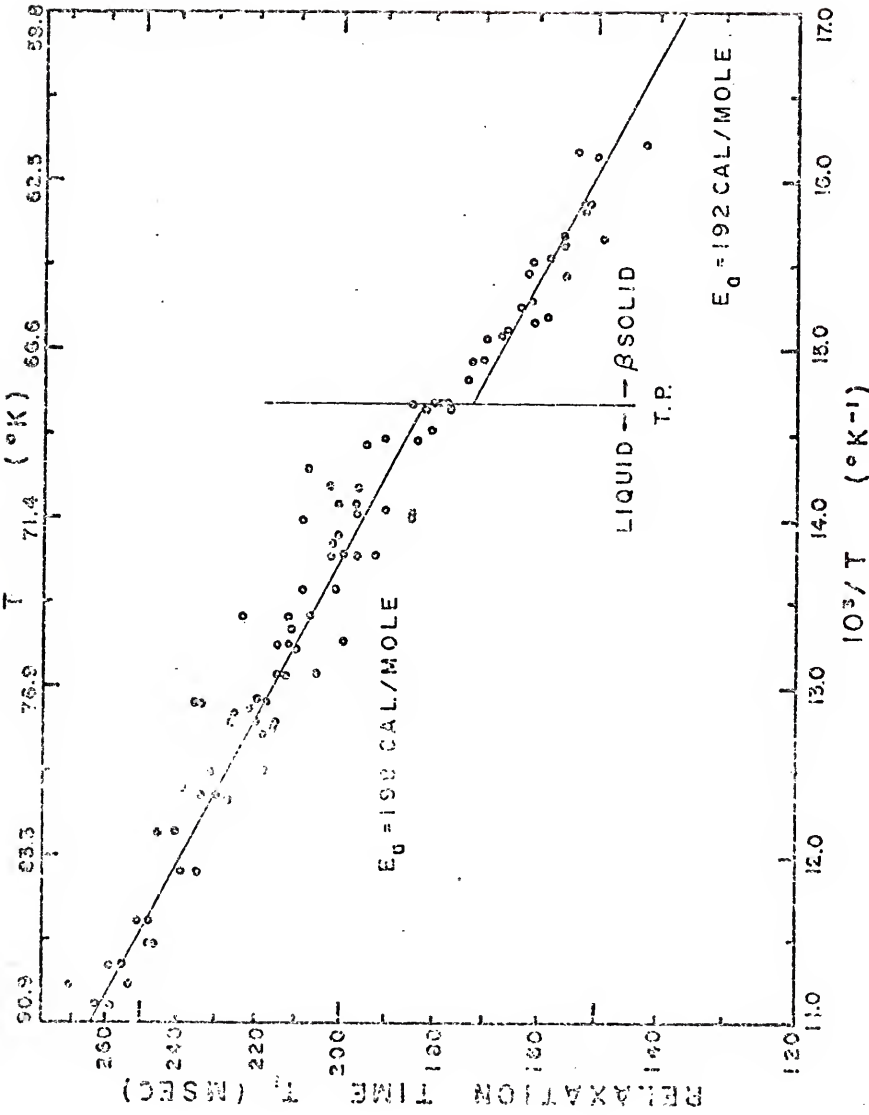


Figure 3-1. Temperature dependence of the spin-lattice relaxation time T_1 of O^{17} in liquid and in β -CO. (E_a is the activation enthalpy. The uncertainty at each measurement is $\pm 10\%$.)

$$\tau_2 = 5.98 \times 10^{-14} \frac{1}{T_1} \quad (3-14)$$

Using (3-14) and measurements of T_1 , the temperature dependence of τ_2 is shown in Figure 3-2. For comparison the τ_2 values of N_2 are shown in this picture [49]. Assuming an activation model [50], such as

$$\tau_2 = \tau_0 e^{\frac{\Delta G}{RT}} \quad (3-15)$$

where ΔG is the difference in the Gibbs function between the initial and activated states, R is the gas constant and τ_0 is a constant and is expected to be a relatively slowly varying function of temperature and pressure [50]. Substituting (3-14) into (3-15) one has

$$T_1 = C e^{\frac{-\Delta G}{RT}} \quad (3-16)$$

where C is some constant. From the thermodynamic relation

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_P \quad (3-17)$$

it follows that

$$\Delta H = -R \left(\frac{\partial \ln T_1}{\partial \left(\frac{1}{T} \right)} \right)_P \quad (3-18)$$

ΔH is the activation enthalpy, a measure of the energy required to re-orient a molecule under conditions of constant pressure. One notes that it is a reasonable approximation to assume that the pressure along the equilibrium vapor pressure curve is constant [50].

3. 5 Discussion

Ewing [7] compared the infrared spectra in the gas and liquid phases of CO and suggested a potential barrier of $V = \frac{1}{2} V_0 (1 - \cos 2\theta)$ with $V_0 = 120$ cal/mole in liquid CO.

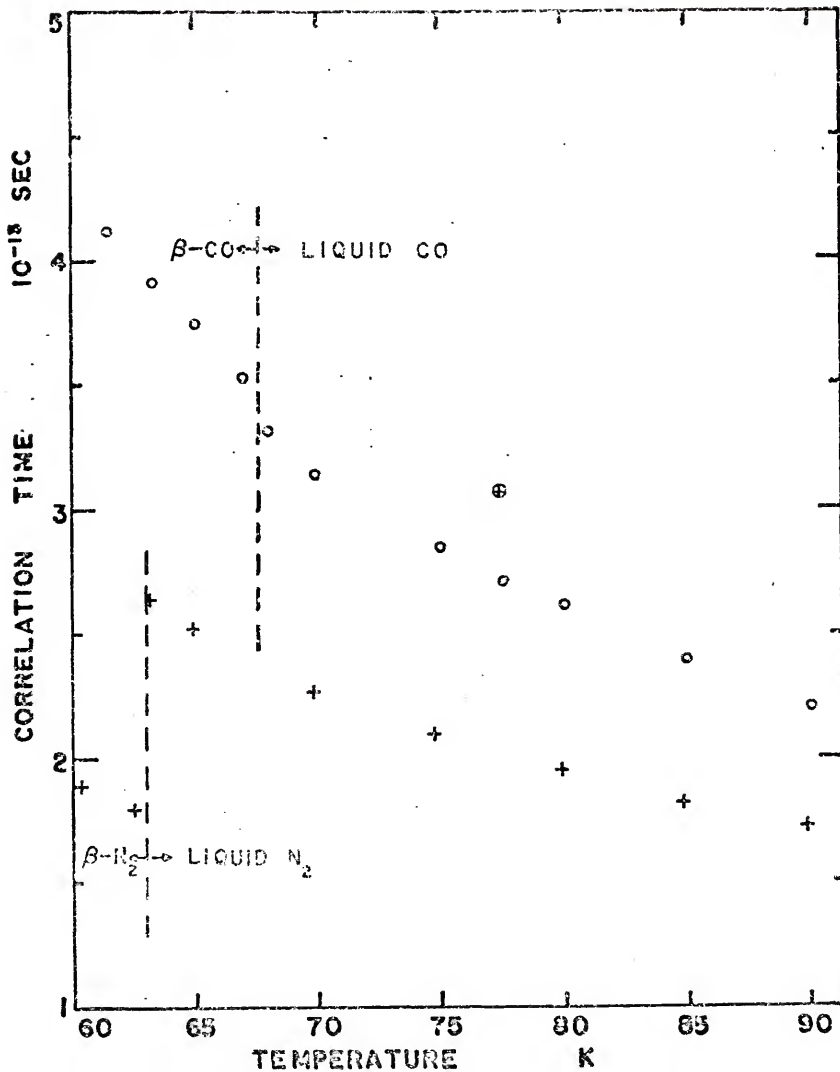


Figure 3-2. Temperature dependence of the autocorrelation time for tumbling rotational motion in liquid CO and for precessional motion in β -CO. (The "o" data are for CO while the "+" data are for N₂ from Ref. [49]. The autocorrelation time in liquid CO and N₂ is shown as "0" from experimental Raman scattering [39]).

Aney [51] used the librational model suggested by Brot and compared this with the far-infrared spectrum of liquid CO and calculated a barrier of 190 cal/mole. These are compared with our experimental activation enthalpy calculated by least square fit to be 198 ± 3 cal/mole. Considering the different types of experiments, it can be regarded as satisfactory. In fact, NMR T_1 measures the barrier height directly and this value is more fundamental than the other parameters. The low value of the barrier potential indicates that CO molecules in the liquid phase undergo nearly free rotation.

If one uses the experimental results for the coefficients of diffusion in liquid CO [46] and assumes a Debye model of viscous fluids, the Stokes-Einstein equation yields

$$\tau = \frac{2a^2}{9D} \quad (3-19)$$

from which it can be calculated that at 77 K, $\tau \approx 2.8 \times 10^{-12}$ sec. This may be compared with the value of $\tau \approx 2.7 \times 10^{-13}$ sec. derived from the T_1 measurements. In liquid N_2 it was found also that use of the Stokes formula for the reorientational correlation time overestimated the value by one order of magnitude [49].

CHAPTER IV SOLID β -PHASE

4. 1 Quadrupole Perturbed NMR Spectra

The hexagonal crystal structure of β -CO has already been discussed in 1. 1. 1. However, the inability of X-ray diffraction to distinguish between a static disorder and a free precession model has led to some confusion in the literature [20].

The experimental data presented here are consistent with the precession model. It is concluded from these experimental NMR measurements that the effective nuclear quadrupole coupling constant of O^{17} in β -CO is reduced by a factor of $\sim 10^{-3}$ by motional averaging. This demonstrates that the molecular motions in β -CO are characterized by a time shorter than the reciprocal of the static quadrupole resonance frequency, $\sim 10^{-6}$ sec., and that the reorientations are not isotropic because a non-zero coupling constant exists. The Hamiltonian of the O^{17} nuclei in β -CO can be written as

$$H = H_Z + H_Q \quad (4-1)$$

where H_Z represents the Zeeman energy while H_Q , the quadrupole Hamiltonian, is small compared to H_Z and can be treated as a perturbation. To a first approximation, the shift in frequency of state $|m\rangle$ can be written as

$$\Delta\nu_m = \frac{1}{h} \left\langle m \left| \frac{eQ}{4I(2I-1)} V_{zz} (3I_z^2 - I^2) \right| m \right\rangle \quad (4-2)$$

where $|m\rangle$ are the eigenstates of Zeeman energy and m is the magnetic quantum number of the nuclear spin O^{17} . V_{zz} is the electric field

gradient at the O^{17} nuclear site in the laboratory frame. From (4-2), knowing $I = \frac{5}{2}$ for O^{17} , one has

$$\Delta v_m = \frac{1}{h} \frac{eQ}{40} V_{ZZ} \left(3m^2 - \frac{35}{4} \right) \quad (4-3)$$

In order to relate the V_{ZZ} in the laboratory frame to the static value of the field gradient V_{ZZ} in the molecular frame, one considers the precessional motion shown in Figure 4-1. In the case $\eta = 0$, the second order irreducible tensor transformation enables one to have

$$V_{ZZ} = \frac{1}{2} (3 \cos^2 \theta'' - 1) V_{ZZ} \quad (4-4)$$

where V_{ZZ} is the static electric field gradient in the molecular frame, while θ'' is the instantaneous angle between the molecular axis and the external magnetic field $\vec{H}_0$. One also assumes the field gradient is of intramolecular origin. If one applies the addition theorem, (4-4) can be written as

$$V_{ZZ} = \frac{1}{4} (3 \cos^2 \theta' - 1) (3 \cos^2 \theta - 1) V_{ZZ} \quad (4-5)$$

The effective V_{ZZ} would be given by the time average of the right hand side of (4-5)

$$\begin{aligned} \overline{V_{ZZ}} &= \frac{1}{4} \overline{(3 \cos^2 \theta' - 1) (3 \cos^2 \theta - 1)} V_{ZZ} \\ &= \frac{1}{4} \overline{(3 \cos^2 \theta' - 1) (3 \sin^2 \gamma \cos^2 \phi - 1)} V_{ZZ} \end{aligned} \quad (4-6)$$

It turns out from (4-3) and (4-6) that

$$\Delta v_m = \frac{1}{h} \frac{e^2 Qq}{160} \overline{(3 \cos^2 \theta' - 1) (3 \sin^2 \gamma \cos^2 \phi - 1)} \left(3m^2 - \frac{35}{4} \right) \quad (4-7)$$

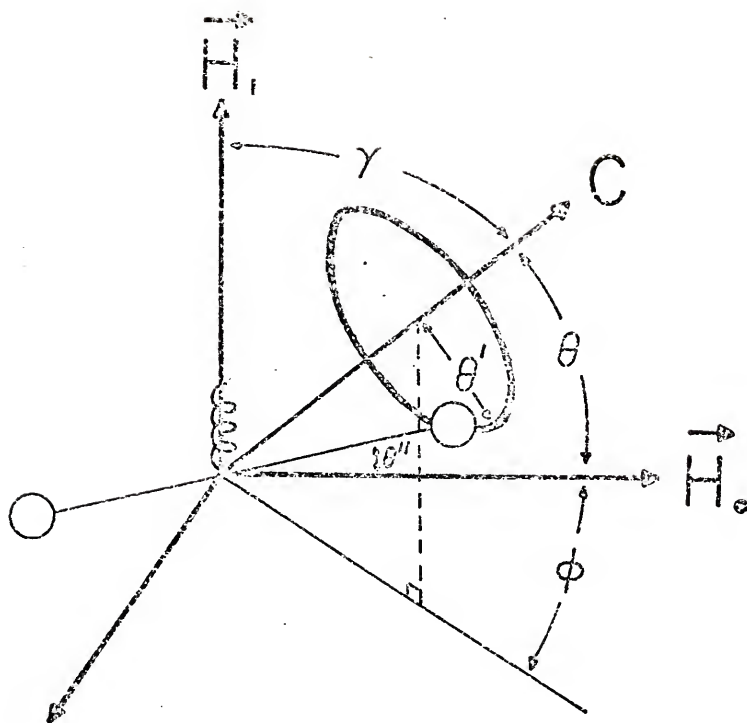


Figure 4-1. Definition of angular variables used in the text to discuss the NMR rotation patterns in β -CO. The molecule is described classically as precessing rapidly about the crystal C axis. $\vec{H}_1$ is the field produced by the rf coil. $\vec{H}_0$ is the externally applied magnetic field. ϕ is the angle between $\vec{H}_0$ and the projection of the C axis on the plane perpendicular to $\vec{H}_1$.

and for various m one can immediately write

$$\overline{\Delta v_{\pm 5}} = \frac{e^2 Q q}{16h} (3 \cos^2 \theta' - 1) (3 \sin^2 \gamma \cos^2 \phi - 1) \quad (4-8)$$

$$\overline{\Delta v_{\pm 3}} = - \frac{e^2 Q q}{80h} (3 \cos^2 \theta' - 1) (3 \sin^2 \gamma \cos^2 \phi - 1) \quad (4-8')$$

$$\overline{\Delta v_{\pm 1}} = - \frac{e^2 Q q}{20h} (3 \cos^2 \theta' - 1) (3 \sin^2 \gamma \cos^2 \phi - 1) . \quad (4-8'')$$

The quadrupole splitting is of the order of KHz while the static quadrupole coupling constant is of the order of MHz. This small non-zero quadrupole frequency might result from a value of θ' close to the magic angle θ_0 , where $3 \cos^2 \theta_0 = 1$. One supposes θ' is characterized by a distribution function $f(\epsilon)$, where $\epsilon = \theta' - \theta_0$, which is an even function of ϵ and normalized. It follows that

$$\begin{aligned} 3 \cos^2 \theta' - 1 &= \int_{-\pi/2}^{\pi/2} f(\epsilon) [3 \cos^2 (\theta_0 + \epsilon) - 1] d\epsilon \\ &= \frac{1}{2} \int_{-\pi/2}^{\pi/2} f(\epsilon) [3 \cos^2 (\theta_0 + \epsilon) - 1 + 3 \cos^2 (\theta_0 - \epsilon) - 1] d\epsilon \\ &= \int_{-\pi/2}^{\pi/2} f(\epsilon) \epsilon^2 d\epsilon \\ &= \epsilon_0^2 \end{aligned} \quad (4-9)$$

where ϵ_0 is the root mean square of the angle ϵ , i.e. θ' derivated from magic angle θ_0 . One defines

$$\mp \overline{\Delta v_{\pm 3}} \pm \overline{\Delta v_{\pm 5}} = \pm v^{(2)} \quad (4-10)$$

and

$$\mp \overline{\Delta v_{\pm 1}} \pm \overline{\Delta v_{\pm 3}} = \pm v^{(1)} . \quad (4-10')$$

And combining (4-8) (4-9), (4-10) and (4-10'), it follows that

$$v^{(2)} = \frac{6e^2 Qq}{80h} \epsilon_0^2 (3 \sin^2 \gamma \cos^2 \phi - 1) \quad (4-11)$$

and

$$v^{(1)} = \frac{3e^2 Qq}{80h} \epsilon_0 (3 \sin^2 \gamma \cos^2 \phi - 1) \quad (4-11')$$

From the experimental perturbed spectra it is obvious that in several cases a large portion of the sample grew as a single crystal of β -CO.

The evidence comes from the rotation patterns of the separations of the satellites as shown in Figure 4-2, in this case at 64.7 K. The perturbed spectra at different angles are also shown in Figure 4-3. One notes that the linewidths are mainly due to the inhomogeneity of the applied magnetic field. Since the separation between $m = +\frac{5}{2}$ and $m = +\frac{3}{2}$ and that between $m = -\frac{5}{2}$ and $m = -\frac{3}{2}$ are symmetric, from the spectra one can only determine

$$\left| 2v^{(2)} \right| = \frac{6}{40} \frac{e^2 Qq}{h} \epsilon_0^2 \left| 3 \sin^2 \gamma \cos^2 \phi - 1 \right| \quad (4-12)$$

and

$$\left| 2v^{(1)} \right| = \frac{3}{40} \frac{e^2 Qq}{h} \epsilon_0^2 \left| 3 \sin^2 \gamma \cos^2 \phi - 1 \right| \quad (4-12')$$

Noting that $|2v^{(2)}| = 2 |2v^{(1)}|$ while one measures $|2v^{(1)}|$, the measurement of $|2v^{(2)}|$ can be used as a supplement to check the accuracy of the $|2v^{(1)}|$ measurement. However, the rotation of the $\vec{H}_0$ field at an angle $\phi = \frac{\pi}{2}$ would give $|3 \sin^2 \gamma \cos^2 \phi - 1| = 1$, while at an angle of ϕ shifted by $\frac{\pi}{2}$ more would give $|3 \sin^2 \gamma \cos^2 \phi - 1| = |3 \sin^2 \gamma - 1|$. It is obvious for symmetry reasons that the rotation pattern of (4-12') as shown in Figure 4.2 is a periodic function of π , having two local maxima. As in Figure 4.2 it is at $\phi - \phi_0 = 32^\circ$, where ϕ_0 is a laboratory reference angle, that gives $\phi = \frac{\pi}{2}$. At this angle (4-11) and (4-11') can be simplified as

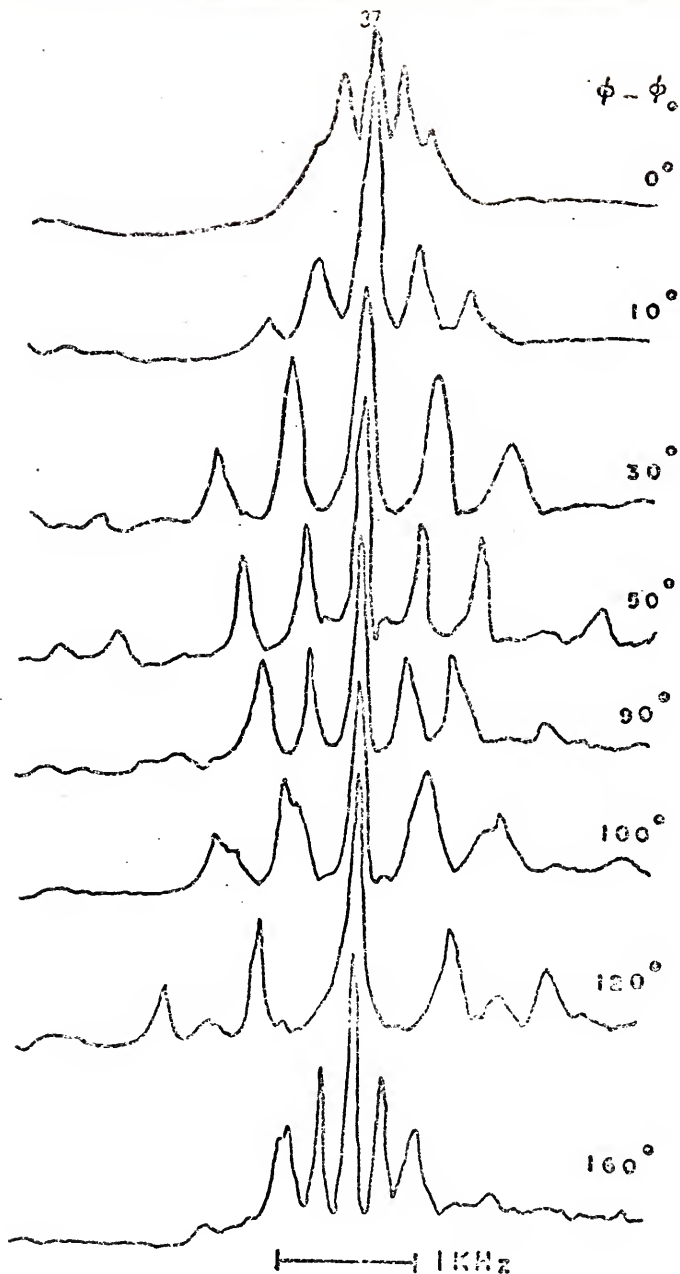


Figure 4-2. The NMR perturbed spectra of β -CO at different $(\phi - \phi_0)$ angles, where ϕ_0 is a laboratory reference angle.

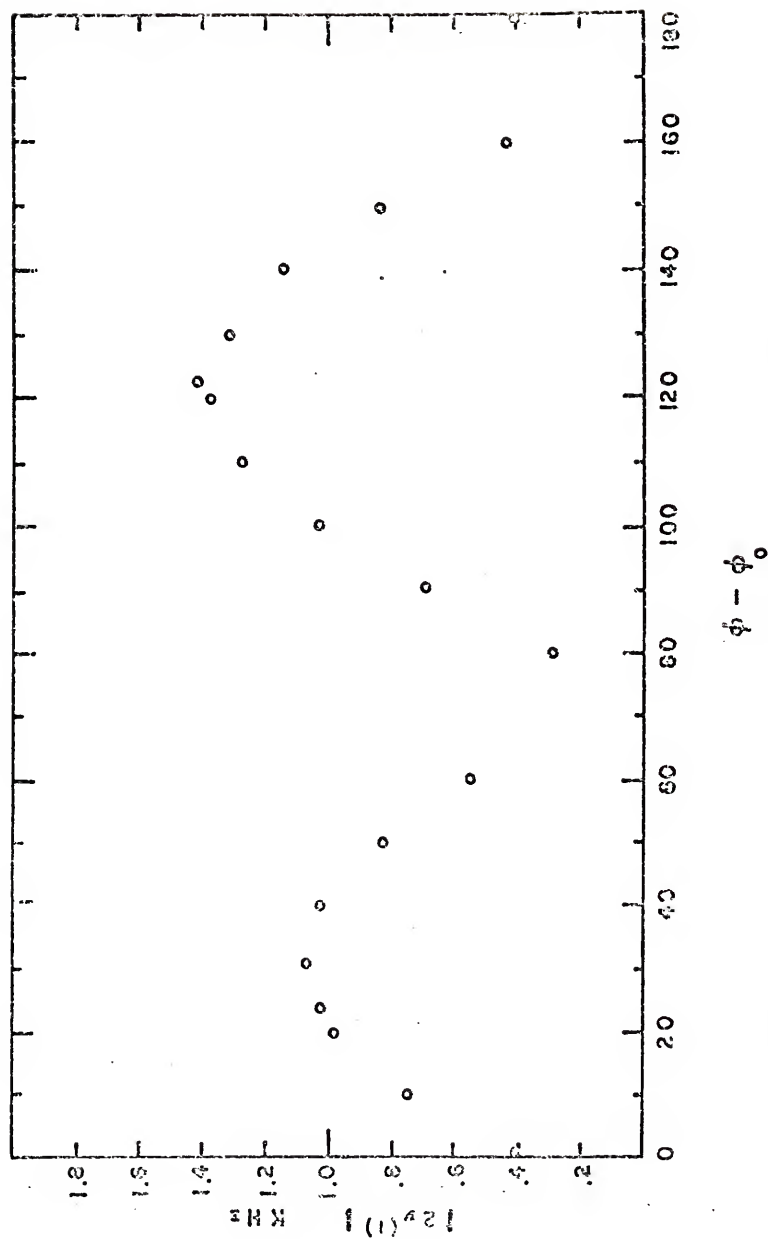


Figure 4-3. Rotation pattern of the separations of the satellites of NMR perturbed spectra in β -CO as a function of $(\phi - \phi_0)$.

$$\left| 2\nu^{(2)} \right| = \frac{6}{40} \frac{e^2 Q q}{h} \epsilon_0^2 \quad (4-13)$$

and

$$\left| 2\nu^{(1)} \right| = \frac{3}{40} \frac{e^2 Q q}{h} \epsilon_0^2 \quad (4-13')$$

In fact the values of $|3 \sin^2 \gamma \cos^2 \phi - 1|$ as a function of ϕ have two local maxima. For $\frac{2}{3} \leq \sin^2 \gamma \leq 1$ the first (larger) maximum located at $\phi = 0^\circ$ while for $0 \leq \sin^2 \gamma \leq \frac{2}{3}$ it is at $\phi = 90^\circ$ [49].

Comparing with different single crystals, it is possible to determine which maximum corresponds to $\phi = 90^\circ$ so that

$$|3 \sin^2 \gamma \cos^2 \phi - 1| = 1 \quad (4-14)$$

It is clear that one can also have an angle ϕ' such that

$$3 \sin^2 \gamma \cos^2 \phi' = 1$$

From (4-14) one determines

$$\sin \gamma = \pm \frac{1}{\sqrt{3}} \frac{1}{\cos \phi'} \quad (4-15)$$

From the experimental value of $|2\nu^{(1)}|$ and the value of the static quadrupole coupling constant which one found in the NQR measurements in α -CO one can determine the value of ϵ_0 . If one defines the effective quadrupole coupling constant as

$$\begin{aligned} \left\langle \frac{e^2 Q q}{h} \right\rangle_{\text{eff}} &= \frac{eQ}{h} v_{ZZ} \frac{1}{2} \sqrt{3 \cos^2 \theta' - 1} \\ &= \frac{e^2 Q q}{2h} \epsilon_0^2 \end{aligned} \quad (4-16)$$

one would have from (4-12), (4-12') and (4-14)

$$\left| 2\nu^{(2)} \right| = \frac{6}{20} < \frac{e^2 Q q}{h} >_{\text{eff}} \quad (4-17)$$

and

$$\left| 2\nu^{(1)} \right| = \frac{3}{20} < \frac{e^2 Q q}{h} >_{\text{eff}} \quad (4-17')$$

The experimental data from the separations of the satellites give

$$< \frac{e^2 Q q}{h} >_{\text{eff}} = 7.04 \text{ KHz} \quad \text{at} \quad T = 64.7 \text{ K} \quad .$$

Comparing this data with the static quadrupole coupling constant of 3.83 MHz one finds that

$$< \frac{e^2 Q q}{h} >_{\text{eff}} = 1.67 \times 10^{-3} \frac{e^2 Q q}{h} \quad (4-18)$$

which is three orders of magnitude smaller. Figure 4-4 shows the effective quadrupole coupling constant for several temperatures of β -CO. With increased temperature one expects ϵ_0 to increase, causing the effective quadrupole coupling to increase with temperature. This is consistent with the experimental results where $\epsilon_0 = 3.23^\circ \pm 0.06^\circ$ at $T \approx 62 \text{ K}$ and $\epsilon_0 = 3.36 \pm 0.06^\circ$ at $T \approx 68 \text{ K}$ near the triple point.

4. 2 T_1 Measurements in β -CO

It is shown in Appendix B that if all lines in the perturbed spectrum are saturated and one assumes $W_1 = W_2$ where

$$W_1 = \frac{W_5}{2} \rightarrow \frac{3}{2} \quad (4-19)$$

$$W_2 = 2\frac{W_5}{2} \rightarrow \frac{1}{2} \quad (4-19')$$

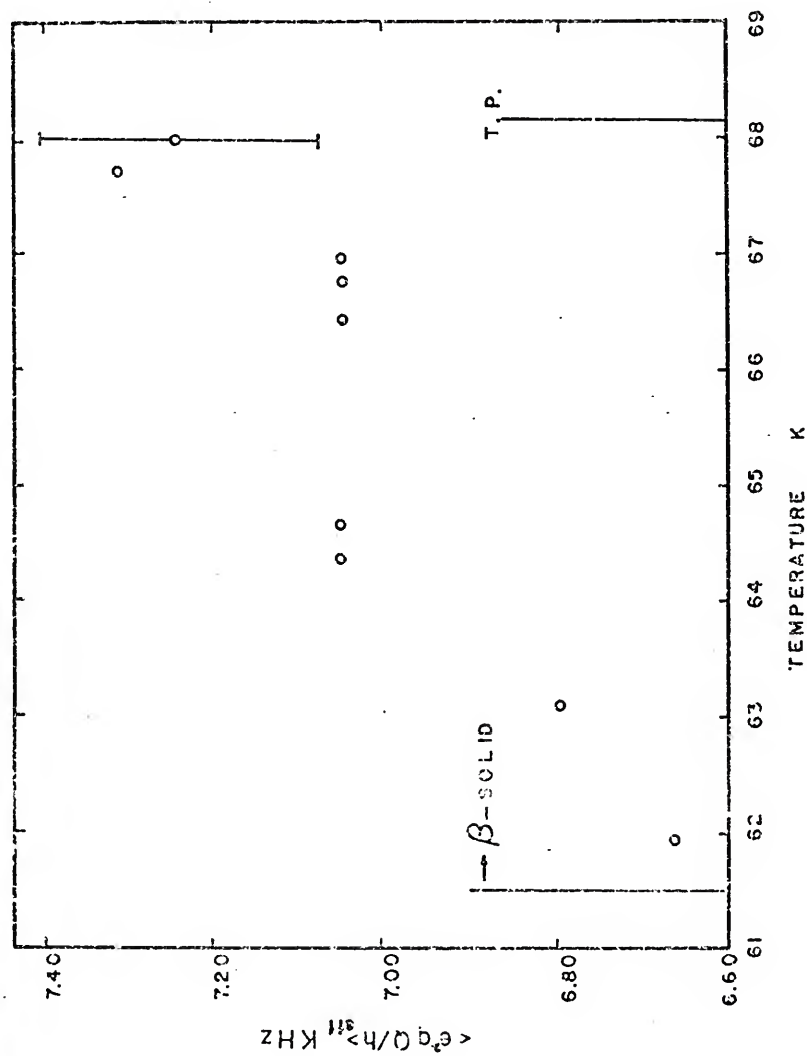


Figure 4-4. Effective coupling constant as a function of temperature in p-CO. (A typical error bar is shown at $T = 68$ K.)

then the spin-lattice relaxation is governed by a single exponential decay

$$\frac{1}{T_1} = \frac{4}{5} W_1 \quad (4-20)$$

In the course of the experiment a sequence of 16 pulses was applied before a $\frac{\pi}{2} - \tau - \frac{\pi}{2}$ pulse sequence was employed to measure the spin-lattice relaxation time. It was found that within experimental error the nuclear magnetization recovered as a single exponential. Furthermore the normal $\frac{\pi}{2} - \tau - \frac{\pi}{2}$ pulse sequence would give an almost identical result except for very small τ . This may come from the small separations between all lines and a $\frac{\pi}{2}$ pulse would suffice to saturate all the lines. The single exponential decay supports our assumption of $W_1 = W_2$. Following the same step as in liquid CO, and assuming the relaxation is dominated by the intramolecular quadrupole interaction, one has

$$\frac{1}{T_1} = \frac{3}{125} \left(\frac{e^2 Q q}{h} \right)^2 \tau_2' \quad (4-21)$$

where τ_2' now is the autocorrelation time for the precessional motion around the crystal C axis. Using $\frac{e^2 Q q}{h}$ from NQR measurements in the α -phase one has the following relation between T_1 and τ_2' :

$$\tau_2' = 5.93 \times 10^{-14} \frac{1}{T_1} \quad (4-22)$$

Shown in Figure 3-2 is the temperature dependence of τ_2' and τ_2 . Although there is a different meaning for τ_2' and τ_2 , they specify the correlational motions in β -phase and liquid CO respectively. Figure 3-2 shows that there is a discontinuity at the transition temperature. It is reasonable that the characteristic time of the motions in β -CO takes a longer period than that in liquid CO, while the discontinuity in the opposite sense of

β -N₂ near the transition temperature is not clear at this moment [52].

For β -N₂ the same assumptions were made as one did in β -CO, namely that

$W_1 = W_2$ and that all lines are saturated. One therefore has

$$\frac{1}{T_1} = 5W_1 \quad (4-23)$$

in liquid N₂ as well as in β -N₂.

CHAPTER V SOLID α -PHASE

5. 1 Molecular Properties of α -CO

Solid α -CO is one of the simplest diatomic molecular crystals and has been an interesting subject for studying the lattice dynamics of molecular crystals [6,11,12,53-55]. The crystal structure has been discussed in 1. 1. 1. One notes that in the face center cubic crystal structure the locations of the molecules and the different orientations along the diagonal can be related to the molecular dipole-dipole and quadrupole-quadrupole electrostatic energies for the various pair orientations [15]. The specific heat study of CO by Clayton and Giauque [4] observed a residual entropy of approximately $R \ln 2$ at low temperatures of α -CO. Gill and Morrison [10] extended the measurements down to 2.5 K with no indication of the occurrence of an order-disorder transition. However, it can be mentioned that a small anomaly has been observed in the heat capacity of α -CO near 18 K and ascribed to the freezing-in of molecular head-to-tail reorientation [16].

5. 2 Nuclear Quadrupole Resonance in α -CO

To study the molecular dynamics in α -CO, one can employ the O^{17} nuclear quadrupole resonance, since the quadrupole coupling constant is large enough to be able to observe the NQR frequency directly. For O^{17} in α -CO intermolecular contributions to the field gradient are very small compared to the intramolecular interactions. Each molecule can therefore be regarded as an isolated spin system. The electric field

gradient (EFG) tensor at the nuclear site is thus axially symmetric and the molecules in α -CO differ little from that in the gas phase. The quadrupole Hamiltonian can be written as

$$H_Q = \frac{e^2 Q q(T)}{4I(2I-1)} [3I_z^2 - I^2] \quad (5-1)$$

where $eq(T)$ is the time average of the principal component of the EFG tensor taken over the vibrational states at temperature T and eQ is the nuclear quadrupole moment. It follows that

$$\frac{\omega_5}{\pm \frac{5}{2}} \leftrightarrow \pm \frac{3}{2} = \frac{3}{10} \frac{e^2 Q q(T)}{h} \quad (5-2)$$

$$\frac{\omega_3}{\pm \frac{3}{2}} \leftrightarrow \pm \frac{1}{2} = \frac{3}{20} \frac{e^2 Q q(T)}{h} \quad (5-3)$$

The zero temperature NQR frequency would in turn determine the static quadrupole coupling constant (QCC). Since by extrapolating the NQR frequency to 0 K one gets

$$\frac{\omega_5}{\pm \frac{5}{2}} \leftrightarrow \pm \frac{3}{2} = 1.15 \text{ MHz} \quad .$$

With zero point correction estimated from Raman spectra [55], one obtains

$$\frac{e^2 Q q}{h} \approx 4.20 \text{ MHz} \quad (5-4)$$

The measurements of the NQR frequency versus the temperature are shown in Figure 5-1. The static QCC was also used to derive τ_2 and τ_2' in the liquid and β -phases respectively. The microwave experiment gave 4.43 MHz for $\frac{e^2 Q q}{h}$. This was refined by Flygare and Weiss to be 4.48 MHz by considering in addition the spin-rotation interaction in the microwave spectrum [56]. Since the same averaging factor due to molecular stretching motions may exist in both solid and liquid phases, the experimental

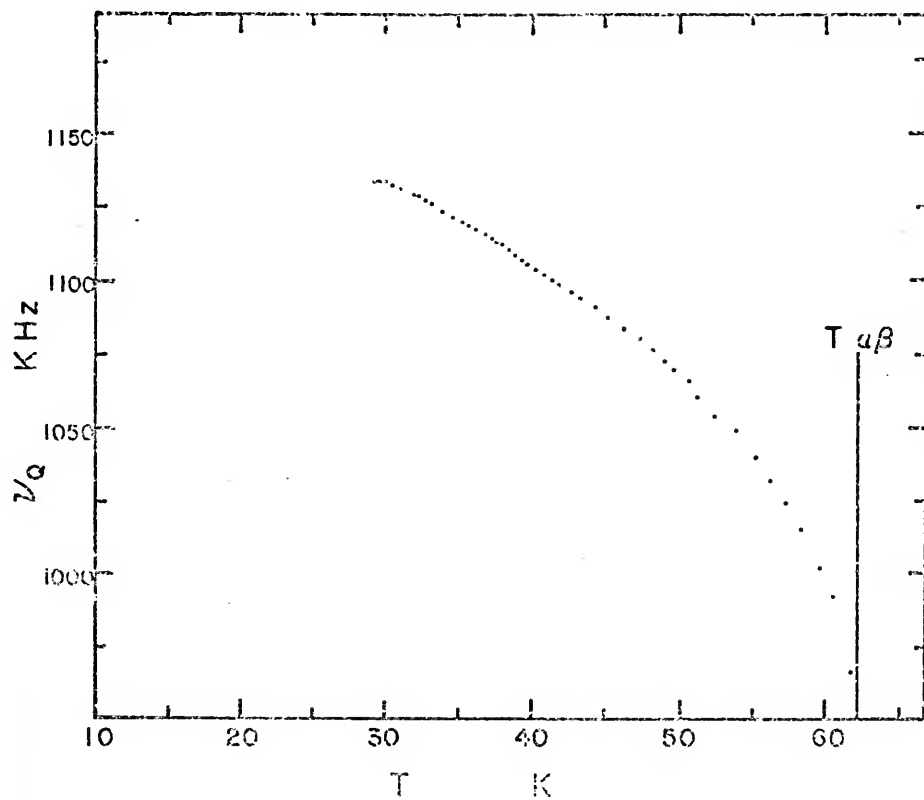


Figure 5-1. Temperature dependence of the pure quadrupole resonance of ^{17}O in $\alpha\text{-CO}$.

NQR determined QCC from the α -phase should be more appropriate for deriving the correlation time of the molecular tumbling motions in the liquid phase.

5. 3 NQR Linewidths and Molecular Motions

The most interesting thing that occurs in the NQR measurements of the α -CO is the anomalous behavior of the linewidths. Figure 5-2 shows the temperature dependence of the linewidths and some T_1 measurements, while Figure 5-3 shows a three dimensional representation of the spectra. As one can see there is a maximum at ~ 37 K and a divergence below ~ 28 K. One might speculate the broadening of the linewidths is related to static effects such as anomalies in the expansion coefficient, metastable states, strains, etc. However, the thermal expansion of α -CO shows no anomalous behavior in this region [18] and the broadening persists for long periods of time (~ 5 hours). As one will see later, the spin-lattice relaxation measurements in the temperature range $48 \sim 60$ K seem to support the hypothesis that the linewidth is actually dominated by the motional contribution.

The occurrence of orientational disorder in the α -CO crystal has been expected since the first estimate of the residual entropy was made [4]. However, the frozen-in static disorder cannot explain the peculiar behavior of the linewidth observed. In the light of the temperature behavior of the O^{17} NQR linewidth and spin-lattice relaxation rates, it will be assumed that the disorder in the orientations of the CO dipoles is of a dynamic nature at least for $T \gtrsim 28$ K.

In the dynamic model one assumes that the molecules execute librational motions around the equilibrium positions plus sudden reorientations among the various directions which are, in principle, permitted by the crystal structure. In order to explain the peculiar behavior of the

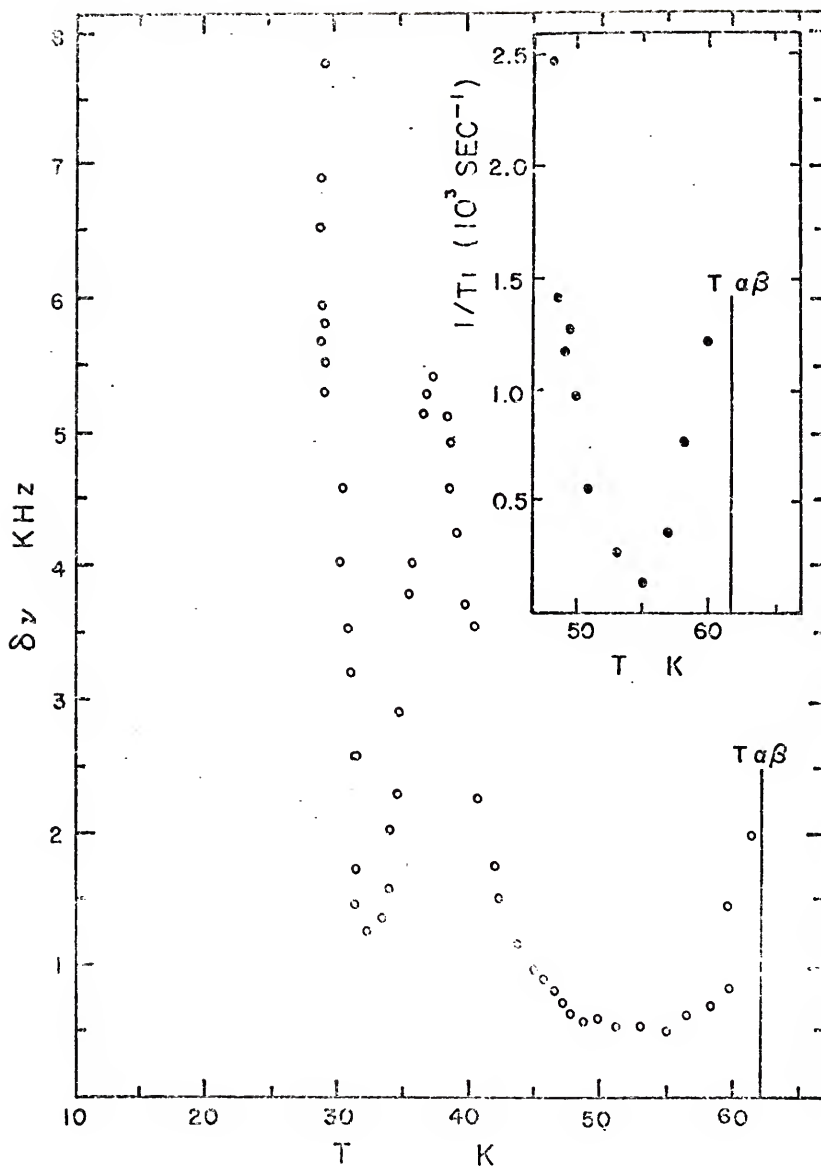


Figure 5-2. Temperature behavior of the O^{17} NQR linewidths in α -CO. The insertion shows some effective T_1 measurements.

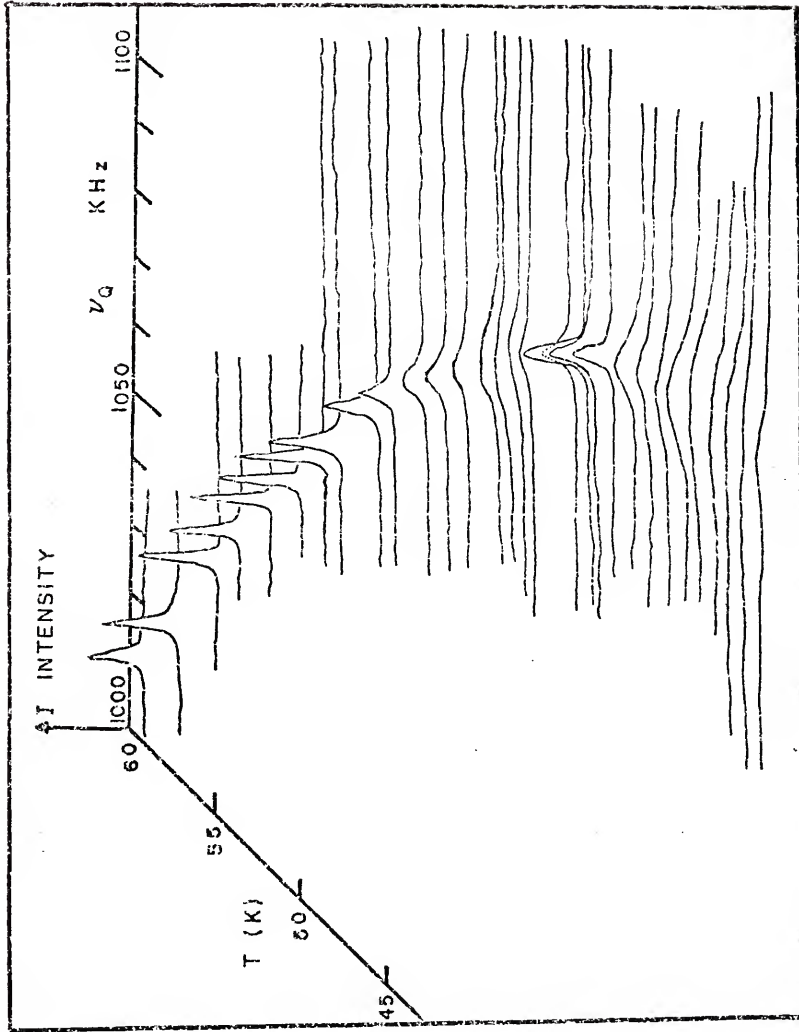


Figure 5-3. Three dimensional representation of the ^{17}O NQR spectra in $\alpha\text{-CO}$. For clarity the linewidth has been enlarged by a factor of 2.

linewidth, that the quadrupole resonance is not affected (normal Bayer type) by the reorientation, one assumes the molecule executes librational motion plus a sudden near π reorientation [57]. In presence of motions, the quadrupole Hamiltonian can be divided into two parts.

$$H_Q = \langle H_Q \rangle + [H_Q - \langle H_Q \rangle] \quad (5-5)$$

The average Hamiltonian $\langle H_Q \rangle$ gives the NQR frequency while the fluctuating part drives the relaxation process and causes the line broadening [58]. For O^{17} in the CO molecule, one assumes a rigid EFG tensor of intramolecular origin with cylindrical symmetry which, as a consequence of motions, moves its principal axes in the laboratory frame. A straightforward tensor transformation gives for the instantaneous EFG components (using $s(t)$ as defined in Appendix C)

$$V_{xx}(t) = -\frac{eq}{2} (1 - 3\phi_1^2) \quad (5-6)$$

$$V_{yy}(t) = -\frac{eq}{2} \left[1 - \frac{3\phi_1^{*2}}{2} (1-s(t)) - 3\phi_1^2 - \frac{3\phi_{11}\phi^*}{2} (1-s(t)) \right]$$

$$V_{zz}(t) = -\frac{eq}{2} \left[-2 + 3\phi_1^2 + 3\phi_{11}^2 + \frac{3\phi_1^{*2}}{2} (1-s(t)) + \frac{3\phi_{11}\phi^*}{2} (1-s(t)) \right]$$

$$V_{xy}(t) = -\frac{3eq}{2} \phi_1 \left[-\frac{\phi^*}{2} (1-s(t)) + \phi_{11} s(t) \right]$$

$$V_{xz}(t) = \frac{3eq}{2} \phi_1 \left[\frac{\phi^{*2}}{4} (1-s(t)) + s(t) + \frac{\phi_{11}\phi^*}{2} (1-s(t)) \right]$$

$$V_{yz}(t) = -\frac{3eq}{2} \left[\frac{\phi^*}{2} (1-s(t)) + \phi_{11} \right]$$

where ϕ_{11} and ϕ_1 are the in-plane and out-of-plane librational angles with respect to the π reorientation respectively. ϕ^* is a random variable of order $\langle \phi_1^2 \rangle^{\frac{1}{2}}$ which allows reversal of an angle which is not exactly π as discussed in [57]. Taking the librational average of (5-6) and assuming no correlation between ϕ_{11} , ϕ_1 and ϕ^* one has

$$\langle V_{xx} \rangle = -\frac{eq}{2} (1 - 3 \langle \phi_1^2 \rangle) \quad (5-7)$$

$$\langle V_{yy} \rangle = -\frac{eq}{2} \left[1 - \frac{3\phi^{*2}}{2} (1 - \langle s(t) \rangle) - 3 \langle \phi_H^2 \rangle \right]$$

$$\langle V_{zz} \rangle = eq \left[1 - \frac{3}{2} \langle \phi_1^2 \rangle - \frac{3}{2} \langle \phi_H^2 \rangle - \frac{3\phi^{*2}}{4} (1 - \langle s(t) \rangle) \right]$$

and

$$\langle V_{xy} \rangle = \langle V_{xz} \rangle = \langle V_{yz} \rangle = 0$$

In the case of disorder, where $\langle s(t) \rangle = 0$, one has

$$\langle V_{zz} \rangle = eq \left(1 - \frac{3}{2} \langle \phi_1^2 \rangle - \frac{3}{2} \langle \phi_H^2 \rangle - \frac{3\phi^{*2}}{4} \right) \quad (5-8)$$

The resonance frequency between $m = \pm \frac{5}{2}$ and $m = \pm \frac{3}{2}$ will be

$$\nu_Q = \frac{3}{10} \frac{e^2 Q q}{h} \left(1 - \frac{3}{2} \langle \phi_1^2 \rangle - \frac{3}{2} \langle \phi_H^2 \rangle - \frac{3}{4} \phi^{*2} \right) \quad (5-9)$$

This is the usual Bayer type NQR frequency. One also notes that for the order phase $\langle s(t) \rangle \neq 0$

$$\nu_Q = \frac{3}{10} \frac{e^2 Q q}{h} \left[1 - \frac{3}{2} \langle \phi_1^2 \rangle - \frac{3}{2} \langle \phi_H^2 \rangle - \frac{3\phi^{*2}}{4} (1 - \langle s(t) \rangle) \right] \quad (5-10)$$

which is higher than in (5-9).

One also notes that if reorientation is sufficiently different from π , i.e. ϕ^* is a large angle, ν_Q would be significantly affected. In order to evaluate the linewidth one considers the fluctuating parts of the components of the EFG tensor from (5-6) and (5-7) and gets

$$V_{xx} - \langle V_{xx} \rangle = \frac{3eq}{2} (\phi_1^2 - \langle \phi_1^2 \rangle) \quad (5-11)$$

$$V_{yy} - \langle V_{yy} \rangle = \frac{3eq}{2} [\phi_{II}^2 - \langle \phi_{II}^2 \rangle - \frac{\phi^{*2}}{2} (s(t) - \langle s(t) \rangle)]$$

$$V_{zz} - \langle V_{zz} \rangle = -\frac{3eq}{2} [\phi_I^2 - \langle \phi_I^2 \rangle + \phi_{II}^2 - \langle \phi_{II}^2 \rangle + \frac{\phi^{*2}}{2} (s(t) - \langle s(t) \rangle)]$$

$$V_{xy} - \langle V_{xy} \rangle = -\frac{3eq}{2} \phi_I [-\frac{\phi^*}{2} (1 - s(t)) - \phi_{II} s(t)]$$

$$V_{xz} - \langle V_{xz} \rangle = \frac{3eq}{2} \phi_I s(t)$$

$$V_{yz} - \langle V_{yz} \rangle = -\frac{3eq}{2} [\frac{\phi^*}{2} (1 - s(t)) + \phi_{II}]$$

There are two parts contributing to the linewidth of the quadrupole resonance, i.e. the adiabatic terms and the nonadiabatic contribution due to the lifetime of the energy levels [58]. One writes

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2} \left(\frac{1}{T_{\pm 5/2}} + \frac{1}{T_{\pm 3/2}} \right) \quad (5-12)$$

where

$$\frac{1}{T_2'} = \int_0^\infty \overline{\omega'(t)\omega'(t-\tau)} d\tau$$

is the adiabatic contribution and $\omega'(t)$ is the departure of the instantaneous resonance from its average value and

$$\frac{1}{T_{\pm 5/2}} = \sum_{m \neq \pm 5/2} W_{\pm 5/2, m} \quad (5-13)$$

$$\frac{1}{T_{\pm 3/2}} = \sum_{m \neq \pm 3/2} W_{\pm 3/2, m} \quad (5-14)$$

where $W_{m,m'}$ is the transition probability per unit time from state m to state m' by the fluctuation terms in (5-11).

By neglecting for simplicity the terms which do not involve the reorientations one would have

$$\frac{1}{T_2} = \left[\frac{9e^2 Qq}{20\hbar} \right]^2 \frac{3 \langle \phi^{*4} \rangle}{16} J_{II}(0) \quad (5-15)$$

where $J_{II}(\omega)$ is the Fourier transform of $\overline{s(t)s(t-\tau)}$. Assuming a harmonic oscillator equation for $\phi_1(t)$ and an exponential correlation function $s(t)$ with characteristic time τ_2' , one has

$$\begin{aligned} \frac{1}{T_{\pm\frac{5}{2}}} = & \left[\frac{9e^2 Qq}{20\hbar} \right]^2 \left[\frac{5 \langle \phi^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} + \frac{20 \langle \phi_1^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + (\omega_1 + \omega)^2 \tau_2'^2} \right. \\ & \left. + \frac{5 \langle \phi^{*4} \rangle}{4} J_{II}\left(\frac{3}{2}\omega\right) \right] \quad (5-16) \end{aligned}$$

where τ_2' is the correlation time for reorientation. ω is the resonance frequency between $m = \pm\frac{5}{2}$ and $m = \pm\frac{3}{2}$. ω_1 is the frequency for the harmonic oscillator $\phi_1(t)$ which is much higher than ω , while

$$\begin{aligned} \frac{1}{T_{\pm\frac{3}{2}}} = & \left[\frac{9e^2 Qq}{20\hbar} \right]^2 \left[\frac{5 \langle \phi^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} + \frac{2 \langle \phi^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + \frac{1}{4}\omega^2 \tau_2'^2} \right. \\ & \left. + \frac{9 \langle \phi^{*4} \rangle}{4} J_{II}\left(\frac{1}{2}\omega\right) \right] \quad (5-17) \end{aligned}$$

Combining (5-15), (5-16) and (5-17) one obtains

$$\begin{aligned} \frac{1}{T_2} = & \left[\frac{9e^2 Qq}{20\hbar} \right]^2 \left[\frac{3 \langle \phi^{*4} \rangle}{16} J_{II}(0) + \frac{9 \langle \phi^{*4} \rangle}{4} J_{II}\left(\frac{1}{2}\omega\right) \right. \\ & + \frac{5 \langle \phi^{*4} \rangle}{4} J_{II}\left(\frac{3}{2}\omega\right) + \frac{10 \langle \phi^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} \\ & \left. + \frac{2 \langle \phi^{*2} \rangle}{9} \frac{\tau_2'^2}{1 + \frac{1}{4}\omega^2 \tau_2'^2} \right] \quad (5-18) \end{aligned}$$

In the fast motion regime, where $J_{II}(0) \approx J_{II}(\frac{1}{2}\omega) \approx J_{II}(\omega) \approx J_{II}(\frac{3}{2}\omega)$, one can neglect terms involving $\langle \phi^{*4} \rangle$, so that (5-18) reduces to

$$\frac{1}{T_2} = \frac{2}{9} \left[\frac{9e^2Qq}{20\hbar} \right]^2 \langle \phi^{*2} \rangle \left[\frac{5\tau_2'}{1 + \omega^2\tau_2'^2} + \frac{4\tau_2'}{4 + \omega^2\tau_2'^2} \right] \quad (5-19)$$

From (5-19), which has a maximum at $\tau_2' \approx 1.188 \frac{1}{\omega}$, one notes that at ~ 37 K the correlation time for reorientation of CO is

$\tau_2' = 1.064 \times 10^{-6}$ sec. The spin-lattice relaxation for NQR with $I = \frac{5}{2}$ is not governed by a single exponential decay [59]. One can define an effective relaxation rate $\left[\frac{1}{T_1} \right]_{\text{eff}}$ which in light of (5-18) one would have

$$\left[\frac{1}{T_1} \right]_{\text{eff}} \approx a \left[\frac{1}{T_2} \right] \quad (5-20)$$

where a is a constant of the order of unity. The measurement of $\left[\frac{1}{T_1} \right]_{\text{eff}}$ in the temperature range of $49 \sim 60$ K supports the hypothesis that the linewidth is due to the motions. In fact, for $T \approx 55$ K one has

$\left[\frac{1}{T_1} \right]_{\text{eff}} = 0.25 \times 10^3 \text{sec}^{-1}$ and according to (5-20) the linewidth should be, for $a = 1$, 0.25 KHz in satisfactory agreement with the experimental result. One notes that a background contribution to the linewidth can be expected from dipolar interactions, strains, and defects, etc. For $T \leq 37$ K the linewidth seem to point out the changeover to a slow motion regime where $\delta\nu$ decreases on cooling. For $\tau_2' \gg \frac{1}{\omega}$ one would have from (5-19)

$$\delta\nu \approx \frac{9}{2\pi} \langle \phi^{*2} \rangle > \frac{1}{\tau_2'} \quad (5-21)$$

It should be pointed out that in the slow motion regime the perturbation approach implicit in the above derivation breaks down. Alexander and Tzalmona [60] showed for slow motions in pure quadrupole resonance, spin-lattice relaxation time and therefore the reversal of the linewidth is

directly proportional to the motional correlation times. It can be speculated that the lack of symmetry of $\delta\nu$ versus T around $T \approx 37$ K is related to the breakdown of the perturbation approach in the slow motion regime.

For temperatures lower than 32 K, $\delta\nu$ exhibits a dramatically increased broadening in a few degrees up to 10 KHz and the NQR signal is no longer detectable below ~ 28 K. Careful attempts for various temperatures down to 4.2 K over a wide range of frequency searching have been unsuccessful.

A possible origin for the behavior of the linewidths could be a change of nature of the reorientations. In particular, the slowing down of motion could favor reorientations from a body diagonal to an equivalent one. As discussed by Rigamonti and Brookeman [61], for a reorientation effectively different from π , one would have

$$\frac{1}{T_1} \sim \delta\nu \sim \omega^2 \tau_2' \quad (5-22)$$

where τ_2' is the fluctuation time between the diagonal equilibrium positions.

This provides one of the explanations of not being able to observe the NQR signal below ~ 28 K. Another possible origin can be found as in α -N₂ where the broadening of lines was characteristic of all mixtures of isotopes and is a consequence of the statistical randomness of the environments of a given type of molecule that produces a dynamic disorder and a local inhomogeneity in the average field gradient [62].

5. 4 Discussion

As shown in Figure 5-4, the temperature dependence of resonance frequency of α -CO is nearly like that of α -N₂, furthermore the reduced NQR frequency $\nu_Q(T) / \nu_Q(0)$ has the value of 0.84 for CO as compared with 0.82 for N₂ at the transition temperature.[49].

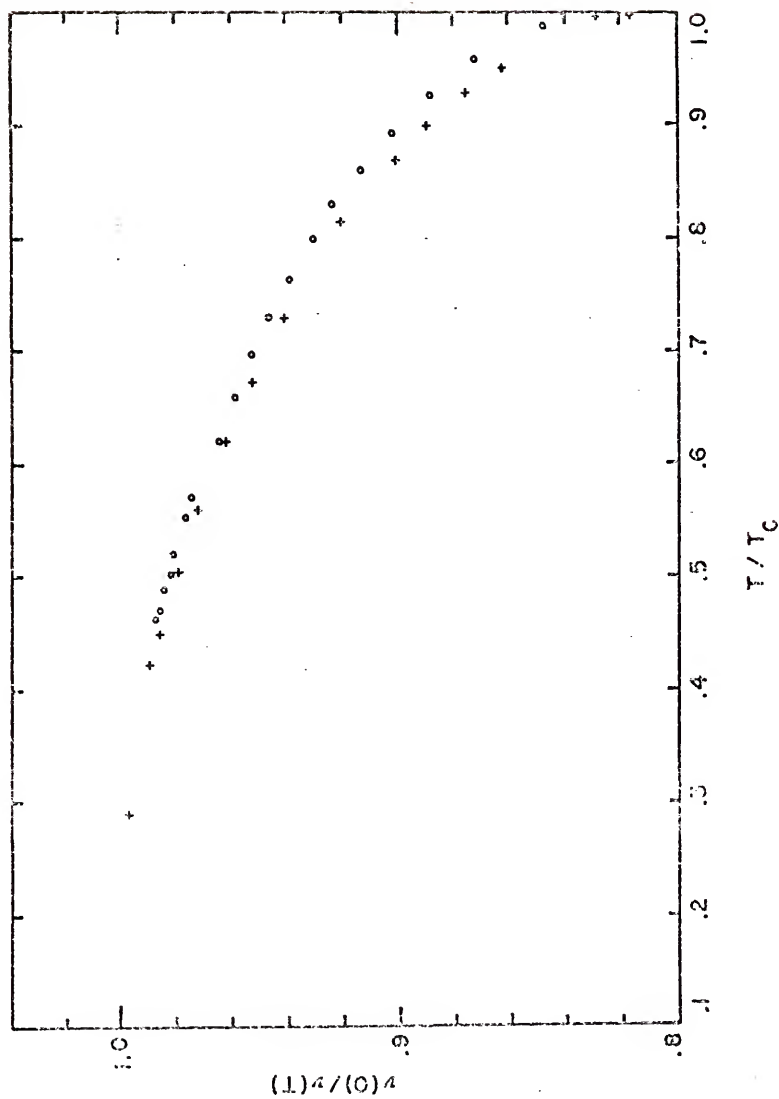


Figure 5-4. The reduced temperature behavior of the reduced NQR frequency. ("o" represents α -CO and "+" represents α -N₂. Data for α -N₂ from Ref. [49]).

The peculiar behavior of the linewidth in the α -phase NQR measurements elucidates the possibility of the motions in α -CO. This is consistent with the observation of the residual entropy. Some $(T_1)_{\text{eff}}$ measurements also support the assumption that motional effects determine the linewidth.

The temperature behavior of $\delta\nu$ between 40 $\sim$ 52 K is satisfactorily fitted by the law

$$\delta\nu \propto e^{\frac{E}{KT}} \quad (5-23)$$

and suggests an activated temperature behavior for τ_2' , with $E \sim 1.2$ K cal/mole.

The assumption of hindered rotation can be ruled out since it would affect resonance frequency by a factor of $\frac{1}{2}$, and this would conflict with the microwave measurements of QCC = 4.4 MHz.

It could also be noted that no reorientation by an angle significantly different from π could be present in the fast motion regime where ($T \geq 37$ K), since the averaging effect would change ν_Q , and this is not observed in the experiment. However, for temperatures $T < 32$ K, it is possible that the reorientation involves angles different from π since in the slow motion regime $\omega\tau_2' \gg 1$ and no average is taken.

The dynamics driving the molecular reorientation should have a cooperative character through the molecular dipole and quadrupole interactions. The correlation time τ_2' introduced above has to be considered a local correlation time driven by the cooperative relaxational time at a given wavevector. Gill and Morrison [10] measured the dielectric constant of α -CO down to 6 K and found no critical effect. This seems to suggest that the characteristic wavevector of the cooperative excitation should be far from zero and the possible phase transition, if any, should be of anti-ferroelectric type.

APPENDIX A
QUADRUPOLE RELAXATION THROUGH MOLECULAR
TUMBLING MOTIONS IN LIQUID CO

In the liquid phase for nuclear spin $I = \frac{5}{2}$, the Zeeman energy levels are all equally spaced. In the absence of an rf field, transitions introduced by the quadrupole interaction are shown in Figure A-1.

The actual values of the transition probabilities depend on the detailed forms of the spectral densities of the field gradients. However, all the upper transition probabilities for $\Delta m = 1$ are simply related to each other. This is also true for $\Delta m = 2$. The quadrupole Hamiltonian can be written as in (1-18)

$$H_Q = \frac{eQ}{4I(2I-1)} \left[\frac{\sqrt{6}}{3} V_0 (3I_z^2 - I^2) + V_+ (I_- I_z + I_z I_-) \right. \\ \left. + V_- (I_+ I_z + I_z I_+) + V_{+2} (I_-)^2 + V_{-2} (I_+)^2 \right] \quad (A-1)$$

where I_+ and I_- are the raising and lowering angular momentum operators respectively. V represents the irreducible field gradient tensor components which are related to the cartesian tensor components by

$$V_0 = \frac{1}{\sqrt{6}} [3V_{zz} - (V_{xx} + V_{yy} + V_{zz})] \quad (A-2)$$

$$V_{\pm 1} = V_{zx} \pm iV_{zy}$$

$$V_{\pm 2} = \frac{1}{2} (V_{xx} - V_{yy}) \pm iV_{xy}$$

One notes that the V_{ij} are symmetric and $V_{xx} + V_{yy} + V_{zz} = 0$. For the raising and lowering operators one has

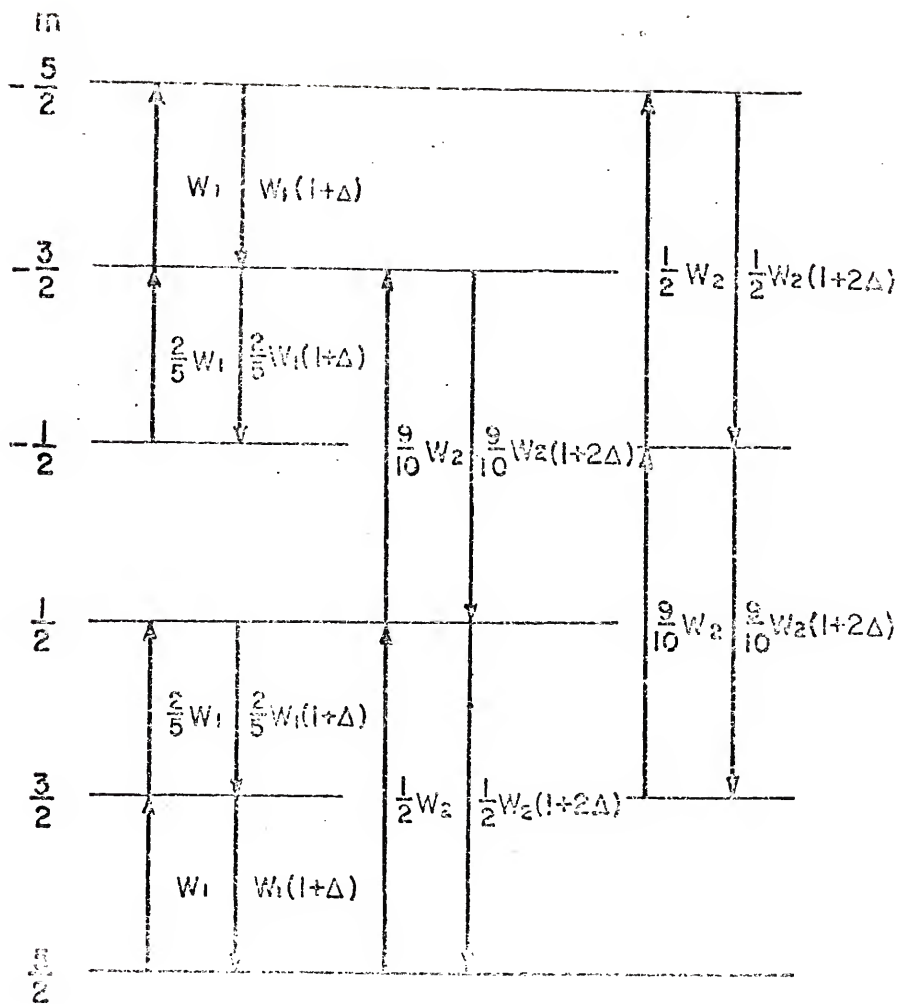


Figure A-1. Quadrupole induced transition probabilities among the Zeeman energy states for spin $I = 5/2$.

$$I_{\pm} I_z \left| I, m \right\rangle = m \sqrt{I(I+1) - m(m\pm 1)} \left| I, m\pm 1 \right\rangle \quad (A-3)$$

and

$$I_z I_{\pm} \left| I, m \right\rangle = (m\pm 1) \sqrt{I(I+1) - m(m\pm 1)} \left| I, m\pm 1 \right\rangle \quad (A-3')$$

One then calculates the matrix elements from (A-3) and (A-3')

$$\left| \left\langle \frac{5}{2}, \pm \frac{5}{2} \right| I_{\pm} I_z + I_z I_{\pm} \left| \frac{5}{2}, \pm \frac{3}{2} \right\rangle \right|^2 = 80 \quad (A-4)$$

$$\left| \left\langle \frac{5}{2}, \pm \frac{3}{2} \right| I_{\mp} I_z + I_z I_{\mp} \left| \frac{5}{2}, \pm \frac{5}{2} \right\rangle \right|^2 = 80$$

and

$$\left| \left\langle \frac{5}{2}, \pm \frac{3}{2} \right| I_{\pm} I_z + I_z I_{\pm} \left| \frac{5}{2}, \pm \frac{1}{2} \right\rangle \right|^2 = 32 \quad (A-4')$$

$$\left| \left\langle \frac{5}{2}, \pm \frac{1}{2} \right| I_{\mp} I_z + I_z I_{\mp} \left| \frac{5}{2}, \pm \frac{3}{2} \right\rangle \right|^2 = 32$$

and also

$$\left| \left\langle \frac{5}{2}, \pm \frac{1}{2} \right| I_{\pm} I_z + I_z I_{\pm} \left| \frac{5}{2}, \mp \frac{1}{2} \right\rangle \right|^2 = 0 \quad (A-4'')$$

For the transitions involving $\Delta m = \pm 2$, one obtains

$$\left| \left\langle \frac{5}{2}, \pm \frac{1}{2} \right| (I_{\pm})^2 \left| \frac{5}{2}, \pm \frac{5}{2} \right\rangle \right|^2 = 40 \quad (A-5)$$

$$\left| \left\langle \frac{5}{2}, \pm \frac{5}{2} \right| (I_{\pm})^2 \left| \frac{5}{2}, \pm \frac{1}{2} \right\rangle \right|^2 = 40$$

and

$$\left| \left\langle \frac{5}{2}, \pm \frac{1}{2} \right| (I_{\pm})^2 \left| \frac{5}{2}, \mp \frac{3}{2} \right\rangle \right|^2 = 72 \quad (A-5')$$

$$\left| \left\langle \frac{5}{2}, \pm \frac{3}{2} \right| (I_{\pm})^2 \left| \frac{5}{2}, \mp \frac{1}{2} \right\rangle \right|^2 = 72$$

From (3-2), (3-4), (A-4) and (A-5) it follows

$$W_1 = \left(\frac{eQ}{\hbar 40} \right)^2 80 \int_{-\infty}^{\infty} e^{-i\omega_L \tau} \overline{V_{+1}(t)} V_{+1}^*(t - \tau) d\tau \quad (A-6)$$

$$W_2 = \left(\frac{eQ}{\hbar 40} \right)^2 80 \int_{-\infty}^{\infty} e^{-i2\omega_L \tau} \overline{V_{+2}(t)} V_{+2}^*(t - \tau) d\tau \quad (A-6')$$

where $W_1 = W_5 \frac{3}{2}, \frac{3}{2}$ and $W_2 = 2W_5 \frac{1}{2}, \frac{1}{2}$. One will need to calculate

$\overline{V_{+1}(t)} V_{+1}^*(t - \tau)$ and $\overline{V_{+2}(t)} V_{+2}^*(t - \tau)$. To do so one considers the irreducible tensor transformation as following. For irreducible tensors V^k of rank k , the $2k + 1$ components of V_p^k are transformed according to the irreducible representation D_k of the rotation group

$$\hat{V}_q^k = \sum_p V_p^k D_{pq}^k(\alpha, \beta, \gamma) \quad (A-7)$$

where (α, β, γ) are the Euler angles of the rotation taking the unprimed reference frame into the primed frame.

The Euler angles are defined by three consecutive rotations: (1) A rotation of angle α about the z axis, (2) A rotation of angle β about the y' axis and (3) A rotation of angle γ about the z'' axis as shown in Figure A-2.

The unitary operator $D(\alpha, \beta, \gamma)$ can be written as

$$D(\alpha, \beta, \gamma) = e^{-i\gamma J_{z''}} e^{-i\beta J_{y'}} e^{-i\alpha J_z} \quad (A-8)$$

Using the fact that

$$J_{y''} = e^{-i\alpha J_z} J_y e^{i\alpha J_z} \quad (A-9)$$

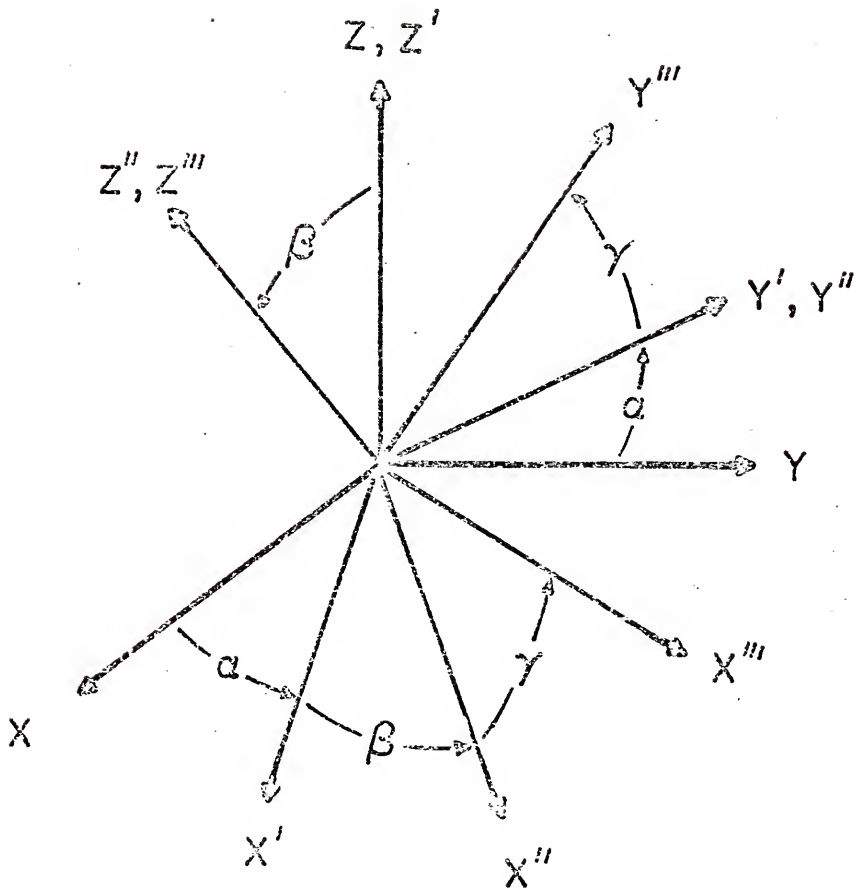


Figure A-2. The Euler angles. First, a rotation of angle α about the Z axis. Secondly, a rotation of angle β about the Y' axis. Finally, a rotation of angle γ about the Z'' axis.

which can be proven as follows. Let $e^{-i\alpha J_z} |a\rangle = |b\rangle$ where $\{|a\rangle\}$ is a complete set of eigenkets before the rotation of α about the z axis, $\{|b\rangle\}$ is another complete set of eigenkets in the coordinate system after rotation. One has

$$\begin{aligned} \langle b' | J_{y'} | b \rangle &= \langle a' | J_y | a \rangle \\ &= \langle a' | e^{i\alpha J_z} J_y e^{-i\alpha J_z} | a \rangle. \end{aligned} \quad (\text{A-10})$$

It follows that

$$J_{y'} = e^{-i\alpha J_z} J_y e^{i\alpha J_z}. \quad (\text{A-11})$$

Using (A-11) and by expanding, it can be proven that

$$e^{-i\beta J_{y'}} = e^{-i\alpha J_z} e^{-i\beta J_y} e^{i\alpha J_z}. \quad (\text{A-12})$$

Following the same procedure, one has

$$e^{-i\gamma J_{z'}} = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} e^{i\beta J_y} e^{i\alpha J_z}. \quad (\text{A-13})$$

From (A-8), (A-12), and (A-13), it can be shown that

$$D(\alpha, \beta, \gamma) = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z}. \quad (\text{A-14})$$

Let $|j, m\rangle$ be a simultaneous eigenket for J^2 and J_z . the matrix elements $D_{m, m'}^j$ then will be written as

$$\begin{aligned} D_{m, m'}^j &= \langle j, m | D(\alpha, \beta, \gamma) | j, m' \rangle \\ &= \langle j, m | e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} | j, m' \rangle \\ &= e^{-i\alpha m} e^{-i\gamma m'} d_{m, m'}^j \end{aligned} \quad (\text{A-15})$$

where the definition of $d_{m, m'}^j$ is obvious.

From the table [30] one has for elements of $d_{m m'}^2(\beta)$ as

$$d_{22}^2 = d_{-2-2}^2 = \cos^4 \left(\frac{\beta}{2} \right) \quad (\text{A-16})$$

$$d_{21}^2 = -d_{12}^2 = -d_{-2-1}^2 = d_{-1-2}^2 = \frac{1}{2} \sin \beta (1 + \cos \beta)$$

$$d_{20}^2 = d_{02}^2 = d_{-20}^2 = d_{0-2}^2 = \sqrt{3/8} \sin^2 \beta$$

$$d_{2-1}^2 = d_{1-2}^2 = -d_{-21}^2 = -d_{-12}^2 = \frac{1}{2} \sin \beta (\cos \beta - 1)$$

$$d_{2-2}^2 = d_{-22}^2 = \sin^4 \left(\frac{\beta}{2} \right)$$

$$d_{11}^2 = d_{-1-1}^2 = \frac{1}{2} (2 \cos \beta - 1) (\cos \beta + 1)$$

$$d_{1-1}^2 = d_{-11}^2 = \frac{1}{2} (2 \cos \beta + 1) (1 - \cos \beta)$$

$$d_{10}^2 = d_{01}^2 = -d_{01}^2 = -d_{10}^2 = -\sqrt{3/2} \sin \beta \cos \beta$$

$$d_{00}^2 = \frac{1}{2} (3 \cos^2 \beta - 1)$$

In the principal reference frame since $V_{ij} = 0$ for $i \neq j$ one would have from (A-2) that

$$V_0 = \frac{3}{\sqrt{6}} V_{ZZ}$$

$$V_{\pm 1} = 0$$

$$V_{\pm 2} = \frac{1}{2} (V_{XX} - V_{YY})$$

Transformation from the principal frame of the field gradient to the laboratory reference frame, yields

$$\begin{aligned}
 V_{+1} = & \frac{3}{\sqrt{6}} V_{ZZ} e^{-i\gamma} \sqrt{3/2} \sin \beta \cos \beta \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{-i2\alpha} e^{-i\gamma} \left[-\frac{1}{2} \sin \beta (1 + \cos \beta) \right] \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{i2\alpha} e^{-i\gamma} \left[-\frac{1}{2} \sin \beta (\cos \beta - 1) \right] \quad (A-17)
 \end{aligned}$$

$$\begin{aligned}
 V_{-1} = & \frac{3}{\sqrt{6}} V_{ZZ} e^{i\gamma} (-\sqrt{3/2} \sin \beta \cos \beta) \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{-i2\alpha} e^{i\gamma} \left[\frac{1}{2} \sin \beta (\cos \beta - 1) \right] \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{i2\alpha} e^{i\gamma} \left[\frac{1}{2} \sin \beta (\cos \beta + 1) \right] \quad (A-17')
 \end{aligned}$$

$$\begin{aligned}
 V_{+2} = & \frac{3}{\sqrt{6}} V_{XX} e^{-i2\gamma} \sqrt{3/8} \sin^2 \beta \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{-i2\alpha} e^{-i2\gamma} \cos^4 \left(\frac{\beta}{2} \right) \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{i2\alpha} e^{-i2\gamma} \sin^4 \left(\frac{\beta}{2} \right) \quad (A-18)
 \end{aligned}$$

$$\begin{aligned}
 V_{-2} = & \frac{3}{\sqrt{6}} V_{ZZ} e^{i2\gamma} \sqrt{3/8} \sin^2 \beta \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{-i2\alpha} e^{i2\gamma} \sin^4 \left(\frac{\beta}{2} \right) \\
 & + \frac{1}{2} (V_{XX} - V_{YY}) e^{i2\alpha} e^{i2\gamma} \cos^4 \left(\frac{\beta}{2} \right) \quad (A-18')
 \end{aligned}$$

If one assumes isotropic motions in the liquid phase and takes the average over all possible orientations one obtains

$$\overline{V_{+1}(t) V_{+1}^*(t)} = \frac{3}{10} \left(1 + \frac{\eta^2}{3}\right) V_{ZZ}^2 \quad (\text{A-19})$$

$$\overline{V_{-1}(t) V_{-1}^*(t)} = \frac{3}{10} \left(1 + \frac{\eta^2}{3}\right) V_{ZZ}^2$$

and

$$\overline{V_{+2}(t) V_{+2}^*(t)} = \frac{3}{10} \left(1 + \frac{\eta^2}{3}\right) V_{ZZ}^2 \quad (\text{A-20})$$

$$\overline{V_{-2}(t) V_{-2}^*(t)} = \frac{3}{10} \left(1 + \frac{\eta^2}{3}\right) V_{ZZ}^2$$

where $\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$ is the asymmetry parameter. Assume

$$\overline{V_i(t) V_i^*(t - \tau)} = |\overline{V_i(t)}|^* e^{-\frac{\tau}{\tau_2}} \quad (\text{A-21})$$

for $i = \pm 1, \pm 2$ where τ_2 characterizes the correlation function of $V_i(t)$.

Using (A-6) and (A-6'), one finds

$$W_1 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 24 \left(1 + \frac{\eta^2}{3}\right) \frac{2\tau_2}{1 + \omega_L^2 \tau_2^2} \quad (\text{A-22})$$

$$W_2 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 24 \left(1 + \frac{\eta^2}{3}\right) \frac{2\tau_2}{1 + 4\omega_L^2 \tau_2^2} \quad (\text{A-22'})$$

In the fast motion regime $\omega_L \tau_2 \ll 1$

$$W_1 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 48 \left(1 + \frac{\eta^2}{3}\right) \tau_2 \quad (\text{A-23})$$

$$W_2 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 48 \left(1 + \frac{\eta^2}{3}\right) \tau_2 \quad (\text{A-23'})$$

The relationship between the experimental T_1 measurement and W_1, W_2 are obtained by considering the rate equations governing the populations among the energy levels.

The number of nuclei in state m has the following time dependence:

$$\frac{dN_m}{dt} = \sum_{m' \neq m} (-N_m W_{m,m'} + N_{m'} W_{m',m}) \quad (A-24)$$

where $W_{m,m'}$ is the transition probability per unit time from state m to state m' , and N_m are the number of nuclei in state m . One can write down all the equations

$$\begin{aligned} \frac{dN_{5/2}}{dt} = & -N_{5/2} W_1 - \frac{1}{2} N_{3/2} W_2 + N_{3/2} W_1 (1 + \Delta) \\ & + \frac{1}{2} N_{1/2} W_2 (1 + 2\Delta) \end{aligned} \quad (A-25)$$

$$\begin{aligned} \frac{dN_{3/2}}{dt} = & -\frac{2}{5} N_{3/2} W_1 - N_{3/2} W_1 (1 + \Delta) - \frac{9}{10} N_{1/2} W_2 \\ & + \frac{2}{5} N_{1/2} W_1 (1 + \Delta) + N_{3/2} W_1 + \frac{9}{10} N_{-1/2} W_2 (1 + 2\Delta) \end{aligned}$$

$$\begin{aligned} \frac{dN_{1/2}}{dt} = & -\frac{2}{5} N_{1/2} W_1 (1 + \Delta) - \frac{1}{2} N_{1/2} W_2 (1 + 2\Delta) - \frac{9}{10} N_{1/2} W_2 \\ & + \frac{2}{5} N_{3/2} W_1 + \frac{1}{2} N_{5/2} W_2 + \frac{9}{10} N_{-3/2} W_2 (1 + 2\Delta) \end{aligned}$$

$$\begin{aligned} \frac{dN_{-1/2}}{dt} = & -\frac{2}{5} N_{-1/2} W_1 - \frac{1}{2} N_{-1/2} W_2 - \frac{9}{10} N_{-1/2} W_2 (1 + 2\Delta) \\ & + \frac{2}{5} N_{-3/2} W_1 (1 + \Delta) + \frac{1}{2} N_{-5/2} W_2 (1 + 2\Delta) + \frac{9}{10} N_{3/2} W_2 \end{aligned}$$

$$\begin{aligned} \frac{dN_{-3/2}}{dt} = & -N_{-3/2} W_1 - \frac{2}{5} N_{3/2} W_1 (1 + \Delta) - \frac{9}{10} N_{-3/2} W_2 (1 + 2\Delta) \\ & + N_{-5/2} W_1 (1 + \Delta) + \frac{2}{5} N_{-1/2} W_1 + \frac{9}{10} N_{1/2} W_2 \end{aligned}$$

$$\frac{dN_{-5/2}}{dt} = -N_{-5/2} W_1 (1 + \Delta) - \frac{1}{2} N_{-5/2} W_2 (1 + 2\Delta) + N_{-3/2} W_1 + \frac{1}{2} N_{-1/2} W_2$$

where the downward transition probability per unit time for $\Delta m = 1$ and $\Delta m = 2$ are given by the upward transition probabilities per unit time multiplied by the Boltzmann factor $1 + \Delta$ and $1 + 2\Delta$ respectively, where $\Delta = \frac{\hbar\omega_L}{KT}$ and one notes $\hbar\omega_L \ll KT$ in the temperature range of interest.

Let $N_{5/2}^0$, $N_{3/2}^0$, and $N_{1/2}^0$ be the number of nuclei in state $m = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$, respectively, at equilibrium with lattice bath. To the first approximation one would have

$$\frac{N_{3/2}}{N_{3/2}^0} (N_{5/2}^0 - N_{3/2}^0) \approx n_0 \Delta \approx N_{5/2}^0 - N_{3/2}^0 \quad (\text{A-26})$$

where $n_0 = \frac{N}{6}$, and N is the total number of nuclei. Similarly,

$$\frac{N_{1/2}}{N_{1/2}^0} (N_{5/2}^0 - N_{1/2}^0) \approx 2n_0 \Delta \approx N_{5/2}^0 - N_{1/2}^0 \quad (\text{A-27})$$

It follows that

$$\begin{aligned} \frac{dN_{5/2}}{dt} = & - (N_{5/2} - N_{5/2}^0) W_1 - \frac{1}{2} (N_{5/2} - N_{5/2}^0) W_2 \\ & + (N_{3/2} - N_{3/2}^0) W_1 + \frac{1}{2} (N_{1/2} - N_{1/2}^0) W_2 . \end{aligned} \quad (\text{A-28})$$

Defining $n_m = N_m - N_m^0$, one can write the following equations from (A-25):

$$\frac{dn_{5/2}}{dt} = -n_{5/2} W_1 - \frac{1}{2} n_{5/2} W_2 + n_{3/2} W_1 + \frac{1}{2} n_{1/2} W_2 \quad (\text{A-29})$$

$$\begin{aligned} \frac{dn_{3/2}}{dt} = & -\frac{2}{5} n_{3/2} W_1 - n_{3/2} W_1 - \frac{9}{10} n_{3/2} W_2 + n_{5/2} W_1 \\ & + \frac{2}{5} n_{1/2} W_1 + \frac{9}{10} n_{1/2} W_2 \end{aligned}$$

$$\begin{aligned}\frac{dn_{1/2}}{dt} = & -\frac{2}{5} n_{1/2} W_1 - \frac{1}{2} n_{1/2} W_2 - \frac{9}{10} n_{1/2} W_2 + \frac{2}{5} n_{3/2} W_1 \\ & + \frac{1}{2} n_{5/2} W_2 + \frac{9}{10} n_{-3/2} W_2\end{aligned}$$

$$\begin{aligned}\frac{dn_{-1/2}}{dt} = & -\frac{2}{5} n_{-1/2} W_1 - \frac{1}{2} n_{-1/2} W_2 - \frac{9}{10} n_{-1/2} W_2 + \frac{2}{5} n_{-3/2} W_1 \\ & + \frac{1}{2} n_{-5/2} W_2 + \frac{9}{10} n_{3/2} W_2\end{aligned}$$

$$\begin{aligned}\frac{dn_{-3/2}}{dt} = & -n_{-3/2} W_1 - \frac{2}{5} n_{-3/2} W_1 - \frac{9}{10} n_{-3/2} W_2 + n_{-5/2} W_1 \\ & + \frac{2}{5} n_{-1/2} W_1 + \frac{9}{10} n_{-1/2} W_2\end{aligned}$$

$$\begin{aligned}\frac{dn_{-5/2}}{dt} = & -n_{-5/2} W_1 - \frac{1}{2} n_{-5/2} W_2 + n_{-3/2} W_1 + \frac{1}{2} n_{-1/2} W_2\end{aligned}$$

By multiplying each equation with the corresponding m and summing all together, one obtains the following equation:

$$\begin{aligned}\frac{d\left\{\langle I_z \rangle - \langle I_z \rangle_0\right\}}{dt} = & -\frac{2}{5} \left\{\langle I_z \rangle - \langle I_z \rangle_0\right\} W_1 - \frac{2}{5} \left\{\langle I_z \rangle - \langle I_z \rangle_0\right\} W_2 \\ & + \left\{\frac{6}{5} n_{3/2} + \frac{3}{5} n_{1/2} - \frac{3}{5} n_{-1/2} - \frac{6}{5} n_{-3/2}\right\} (W_1 - W_2) .\end{aligned}\tag{A-30}$$

To a first approximation and assuming that the spin temperature can be defined, one notes

$$\begin{aligned}\frac{6}{5} n_{3/2} + \frac{3}{5} n_{1/2} - \frac{3}{5} n_{-1/2} - \frac{6}{5} n_{-3/2} & \approx \frac{6}{5} n_0 + \frac{3}{5} n_0 - \frac{3}{5} n_0 - \frac{6}{5} n_0 \\ & + \left(\frac{18}{10} + \frac{3}{10} + \frac{3}{10} + \frac{18}{10}\right) \Delta n_0 \\ & \approx 0\end{aligned}\tag{A-31}$$

where $\Delta' = \frac{\hbar\omega_L}{KT_S}$ and T_S is the spin temperature which is generally greater than the lattice temperature. One then concludes that

$$\frac{d\left(\langle I_Z \rangle - \langle I_Z \rangle_0\right)}{dt} = -\frac{2}{5} \left(\langle I_Z \rangle - \langle I_Z \rangle_0\right) (W_1 + W_2) \quad (\text{A-32})$$

which implies

$$\frac{1}{T_1} = \frac{2}{5} (W_1 + W_2) \quad (\text{A-33})$$

and finally, it follows from (A-23), (A-23) and (A-33) that

$$\frac{1}{T_1} = \frac{3}{125} \left(\frac{e^2 Q q}{\hbar} \right)^2 (1 + n^2) \tau_2 \quad (\text{A-34})$$

in the fast motion regime.

APPENDIX B
NMR SPIN-LATTICE RELAXATION
THROUGH THE QUADRUPOLE INTERACTION IN SOLID β -CO

In solid β -CO, the time averaged quadrupole interaction represents a small perturbation term to the total Hamiltonian and the Zeeman energy levels are unequal. In the absence of spin-exchange transitions, the Boltzmann distribution of the populations among the energy levels cannot be maintained. In such a case the spin-lattice relaxation is, in general, not characterized by a single relaxation rate. In addition, the relative importance of the different relaxation rates depends on the nature of the relaxation processes and on the initial conditions [38]. However, since the quadrupole splittings are small compared with the Zeeman energy levels, this simplifies the problem. Considering for spin $I = \frac{5}{2}$, from (A-25) one has

$$\begin{aligned} \frac{d(N_{5/2} - N_{3/2})}{dt} &= (N_{5/2} - N_{3/2})(-2W_1 - \frac{1}{2}W_2) + \frac{2}{5}(N_{3/2} - N_{1/2})(W_1 + W_2) \\ &\quad + \frac{9}{10}(N_{1/2} - N_{-1/2})W_2 + \frac{4}{5}n_0\Delta(2W_1 - W_2) \end{aligned} \quad (B-1)$$

$$\begin{aligned} \frac{d(N_{3/2} - N_{1/2})}{dt} &= (N_{5/2} - N_{3/2})(W_1 - \frac{1}{2}W_2) - \frac{1}{5}(N_{3/2} - N_{1/2})(4W_1 + 7W_2) \\ &\quad + \frac{9}{10}(N_{-1/2} - N_{-3/2})W_2 - \frac{1}{5}n_0\Delta(W_1 - 5W_2) \end{aligned}$$

$$\begin{aligned} \frac{d(N_{1/2} - N_{-1/2})}{dt} = & \frac{1}{2} (N_{5/2} - N_{3/2}) W_2 + \frac{2}{5} (N_{3/2} - N_{1/2}) (W_1 - W_2) \\ & - \frac{9}{5} (N_{1/2} - N_{-1/2}) W_2 + \frac{2}{5} (N_{-1/2} - N_{-3/2}) (W_1 - W_2) \\ & + \frac{1}{2} (N_{-3/2} - N_{-5/2}) W_2 + \frac{4}{5} n_0 \Delta (2W_2 - W_1) \end{aligned}$$

$$\begin{aligned} \frac{d(N_{-1/2} - N_{-3/2})}{dt} = & (N_{-3/2} - N_{-5/2}) (W_1 - \frac{1}{2} W_2) \\ & - \frac{1}{5} (N_{-1/2} - N_{-3/2}) (4W_1 + 7W_2) \\ & + \frac{9}{10} (N_{3/2} - N_{1/2}) W_2 - \frac{1}{5} n_0 \Delta (W_1 - 5W_2) \end{aligned}$$

$$\begin{aligned} \frac{d(N_{-3/2} - N_{-5/2})}{dt} = & (N_{-3/2} - N_{-5/2}) (-2W_1 - \frac{1}{2} W_2) \\ & + \frac{2}{5} (N_{-1/2} - N_{-3/2}) (W_1 + W_2) \\ & + \frac{9}{10} (N_{1/2} - N_{-1/2}) W_2 + \frac{4}{5} n_0 \Delta (2W_1 - W_2) \end{aligned}$$

where W_1 , W_2 and Δ have the same definitions as in Appendix A. If one now defines $N_{m+1/2} = N_{m+1} - N_m$ from the symmetrical equations above, it follows

$$\begin{aligned} N_2 = & -N_2 (2W_1 + \frac{1}{2} W_2) + \frac{2}{5} N_1 (W_1 + W_2) + \frac{9}{10} N_0 W_2 + \frac{8}{5} n_0 \Delta (W_1 - \frac{1}{2} W_2) \\ N_1 = & N_2 (W_1 - \frac{1}{2} W_2) - \frac{1}{5} N_1 (4W_1 + 7W_2) + \frac{9}{10} N_{-1} W_2 - \frac{1}{5} n_0 \Delta (W_1 - 5W_2) \\ N_0 = & \frac{1}{2} N_2 W_2 + \frac{2}{5} N_1 (W_1 - W_2) - \frac{9}{5} N_0 W_2 + \frac{2}{5} N_{-1} (W_1 - W_2) \\ & + \frac{1}{2} N_{-2} W_2 + \frac{4}{5} n_0 \Delta (-W_1 + 2W_2) \end{aligned}$$

with two symmetric equations for N_{-1} and N_{-2} .

The solutions of these three equations are characterized by only three relaxation times. To simplify the equations in (B-2), one defines

$$N_p' = N_p - n_0 \quad (\text{B-3})$$

where n_0 and Δ have the same meanings as in Appendix A. (B-2) then becomes

$$N_2' = -N_2' (2W_1 + \frac{1}{2} W_2) + \frac{2}{5} N_1' (W_1 + W_2) + \frac{9}{10} N_0' W_2 \quad (\text{B-4})$$

$$N_1' = N_2' (W_1 - \frac{1}{2} W_2) - \frac{1}{5} N_1' (4W_1 + 7W_2) + \frac{9}{10} N_1' W_2$$

$$N_0' = \frac{1}{2} N_2' W_2 + \frac{2}{5} N_1' (W_1 - W_2) - \frac{9}{5} N_0' W_2 + \frac{2}{5} N_1' (W_1 - W_2) + \frac{1}{2} N_2' W_2 .$$

Now assuming a precessional motion in β -CO and for simplicity an axially symmetric field gradient, one can calculate $\overline{|V_i'|^2}$ from (A-17), (A-17'), (A-18) and (A-18') for $i = \pm 1$ and $i = \pm 2$

$$\overline{|V_{\pm 1}'|^2} = \frac{9}{4} \sin^2 \beta \cos^2 \beta V_{ZZ}^2 \quad (\text{B-5})$$

$$\overline{|V_{\pm 2}'|^2} = \frac{9}{16} \sin^4 \beta V_{ZZ}^2 .$$

In chapter III it is shown that

$$3 \cos^2 \beta - 1 \approx 0$$

so that, (B-5) can be reduced to

$$\overline{|V_{\pm 1}'|^2} = \frac{1}{2} V_{ZZ}^2 \quad (\text{B-6})$$

$$\overline{|V_2'|^2} = \frac{1}{4} V_{ZZ}^2$$

$$\overline{|V_0'|^2} = 0$$

where the V terms are the EFG tensor components in the crystal frame, while the tensor transformation from the crystal reference frame to the laboratory frame follows the same procedure as in (A-17) and (A-18).

$$V_{+1} = V_2' D_{21} + V_{-2}' D_{-21} + V_1' D_{11} + V_{-1}' D_{-11} \quad (B-7)$$

$$V_{+2} = V_2' D_{22} + V_{-2}' D_{-22} + V_1' D_{12} + V_{-1}' D_{-12} . \quad (B-7')$$

For a powder sample using (A-16) and (A-18) and taking over all the possible directions, one calculates

$$\overline{|V_{+1}|^2} = \frac{3}{10} V_{ZZ}^2 \quad (B-8)$$

$$\overline{|V_{+2}|^2} = \frac{3}{10} V_{ZZ}^2 . \quad (B-8')$$

The same equations will hold for $\overline{|V_{-1}|^2}$ and $\overline{|V_{-2}|^2}$, assuming again

$$\overline{V_i(t) V_i^*(t - \tau)} = \overline{|V_i(t)|^2} e^{-\frac{\tau}{\tau_2}}$$

for $i = \pm 1, \pm 2$ where τ_2 characterizes the correlational precessional motions. Using (A-6) and (A-6') one obtains

$$W_1 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 48 \frac{\tau_2^2}{1 + \omega_L^2 \tau_2^2} \quad (B-9)$$

$$W_2 = \left(\frac{e^2 Q q}{40 \hbar} \right)^2 48 \frac{\tau_2^2}{1 + 4 \omega_L^2 \tau_2^2} . \quad (B-9')$$

From (B-9) and (B-9') it is obvious that $W_1 \approx W_2$. In the fast precessional motion regime $\omega_L \tau_2^2 \ll 1$. It follows from (B-9) and (B-9') that

$$W_1 = 48 \left(\frac{e^2 Q q}{40 \hbar} \right)^2 \tau_2^2 \quad (B-10)$$

$$W_2 = 48 \left(\frac{e^2 Q q}{40 \hbar} \right)^2 \tau_2^2 . \quad (B-10')$$

That is, $W_1 = W_2$ in the fast motion regime.

Now from (B-4) it is possible to write

$$N_2' = -\frac{5}{2} W_1 N_2' + \frac{4}{5} W_1 N_1' + \frac{9}{10} W_1 N_0' \quad (\text{B-11})$$

$$N_1' = \frac{1}{2} W_1 N_2' - \frac{11}{5} W_1 N_1' + \frac{9}{10} W_1 N_0'$$

$$N_0' = \frac{1}{2} W_1 N_2' - \frac{9}{5} W_1 N_0' + \frac{1}{2} W_1 N_{-2}'$$

Since one considers the initial condition that all lines are saturated, it follows from the symmetric equations that $N_{-1}' = N_1'$ and $N_{-2}' = N_2'$.

(B-11) is further reduced to

$$N_2' = -\frac{5}{2} W_1 N_2' + \frac{4}{5} W_1 N_1' + \frac{9}{10} W_1 N_0' \quad (\text{B-12})$$

$$N_1' = \frac{1}{2} W_1 N_2' - \frac{13}{10} W_1 N_1'$$

$$N_0' = W_1 N_2' - \frac{9}{5} W_1 N_0'$$

The general solutions of (B-12) will be

$$N_p' = a_{p1} e^{-\lambda_1 t} + a_{p2} e^{-\lambda_2 t} + a_{p3} e^{-\lambda_3 t} \quad (\text{B-13})$$

where $p = 0, 1, 2$. Substituting (B-13) into (B-12) and comparing the $e^{-\lambda_1 t}$, $e^{-\lambda_2 t}$ and $e^{-\lambda_3 t}$ terms one has

$$\left(-\frac{5}{2} W_1 + \lambda_1\right) a_{21} + \frac{4}{5} W_1 a_{11} + \frac{9}{10} W_1 a_{01} = 0 \quad (\text{B-14})$$

$$\frac{1}{2} W_1 a_{21} + \left(-\frac{13}{10} W_1 + \lambda_1\right) a_{11} = 0$$

$$W_1 a_{21} + \left(-\frac{9}{5} W_1 + \lambda_1\right) a_{01} = 0$$

and similar equations for $e^{-\lambda_2 t}$ and $e^{-\lambda_3 t}$ terms.

In order that all $a_{ij} \neq 0$ for $i = 0, 1, 2; j = 1, 2, 3$ one needs

$$\begin{vmatrix} -\frac{5}{2} W_1 + \lambda & \frac{4}{5} W_1 & \frac{9}{10} W_1 \\ \frac{1}{2} W_1 & -\frac{13}{10} W_1 + \lambda & 0 \\ W_1 & 0 & -\frac{9}{5} W_1 + \lambda \end{vmatrix} = 0 \quad (\text{B-15})$$

This is reduced to

$$(5\lambda - 4W_1)(2\lambda - 3W_1)(10\lambda - 33W_1) = 0$$

i.e., with solutions

$$\lambda = \frac{4}{5} W_1, \quad \frac{3}{2} W_1, \quad \frac{33}{10} W_1 \quad (\text{B-16})$$

In the case that all the lines are saturated at time zero, one has from (B-3)

$$N_2 = N_1 = N_0 = 0$$

and

$$N_2' = N_1' = N_0' = -n_0 \Delta \quad (\text{B-17})$$

Let $\lambda_1 = \frac{4}{5} W_1$, $\lambda_2 = \frac{3}{2} W_1$ and $\lambda_3 = \frac{33}{10} W_1$. Comparing with terms of $e^{-\lambda t}$, (B-12) gives, at $t = 0$

(B-18)

$$\left(-\frac{17}{10} a_{21} - a_{22} + \frac{8}{10} a_{23}\right) + \frac{4}{5} (a_{11} + a_{12} + a_{13}) + \frac{9}{10} (a_{01} + a_{02} + a_{03}) = 0$$

$$\frac{1}{2} (a_{21} + a_{22} + a_{23}) + \left(-\frac{1}{2} a_{11} + \frac{1}{5} a_{12} + 2a_{13}\right) = 0$$

$$(a_{21} + a_{22} + a_{23}) + \left(-a_{01} - \frac{3}{10} a_{02} + \frac{3}{2} a_{03}\right) = 0.$$

From (B-17) and (B-13) one has at $t = 0$

$$-n_0 \Delta = a_{21} + a_{22} + a_{23} \quad (\text{B-19})$$

$$-n_0 \Delta = a_{11} + a_{12} + a_{13}$$

$$-n_0 \Delta = a_{01} + a_{02} + a_{03}.$$

(B-18) and (B-19) enable one to deduce

$$a_{21} = a_{01} = a_{11} \quad (\text{B-20})$$

$$a_{22} = \frac{3}{10} a_{02} = -\frac{2}{5} a_{12}$$

$$a_{23} = -4 a_{13} = \frac{3}{2} a_{23}$$

which gives

$$a_{21} = a_{11} = a_{01} = -n_0 \Delta$$

and all other $a_{ij} = 0$ for $i = 0, 1, 2$; and $j = 2, 3$. The solutions will then be

$$N_p = n_0 \Delta (1 - e^{-4/5 \lambda W_1 t}) \quad (\text{B-22})$$

for $p = 0, 1, 2$.

Therefore, in the case of complete saturation and $W_1 = W_2$, the spin-lattice relaxation is governed by a single exponential decay having

$$\frac{1}{T_1} = \frac{4}{5} W_1 \quad . \quad (B-23)$$

From (B-10) and (B-23) one has the same equation as in the liquid phase in (A-34)

$$\frac{1}{T_1} = \frac{3}{125} \left(\frac{e^2 Q q}{\hbar} \right)^2 \tau_2' \quad (B-24)$$

where τ_2' is the correlation time for the molecular precessional motions around the crystal C axis.

APPENDIX C LINEWIDTHS AND MOLECULAR MOTIONS IN α -CO

One assumes that the molecules in α -CO execute librational motions and sudden reorientations. The tensor components in the laboratory frame and those in the principal reference frame are related by the rotational operator $R(\alpha, \phi_1)$

$$V_{ij} = R^{-1}(\alpha, \phi_1) V'_{ij} R(\alpha, \phi_1) \quad (C-1)$$

where $R(\alpha, \phi_1) = R_y(\phi_1) R_x(\alpha)$. The V'_{ij} and V_{ij} terms are the EFG tensor components in the principal and laboratory reference frames, respectively. ϕ_1 is the out-of-plane librational angle and α is the reorientational angle.

$$V'_{ij} = \text{eq} \begin{vmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad (C-2)$$

In (C-2) a symmetric field gradient has been assumed. It so happens that by assuming a small angle for ϕ_1 ,

$$V_{xx} = -\frac{\text{eq}}{2} (1 - 3\phi_1^2) \quad (C-3)$$

$$V_{yy} = -\frac{\text{eq}}{2} (1 + 3\phi_1^2 \sin^2 \alpha - 3 \sin^2 \alpha)$$

$$V_{zz} = -\frac{\text{eq}}{2} (1 + 3\phi_1^2 \cos^2 \alpha - 3 \cos^2 \alpha)$$

$$V_{xy} = -\frac{\text{eq}}{2} 3\phi_1 \sin \alpha$$

$$V_{xz} = -\frac{eq}{2} 3\phi_1 \cos \alpha$$

$$V_{yz} = -\frac{eq}{2} 3 \sin \alpha \cos \alpha$$

For a sudden reorientation of an angle from 0 to π as is the case discussed in NaNO_2 by Ambrosetti et al. [57].

$$\alpha = \left(\frac{\pi}{2} + \frac{\phi^*}{2}\right) - \left(\frac{\pi}{2} + \frac{\phi^*}{2}\right) s(t) + \phi_{||} \quad (\text{C-4})$$

where $s(t)$ may take values $+1$ or -1 , and ϕ^* is introduced to account for jumps not exactly equal to π . $\phi_{||}$ is the in-plane librational angle. By assuming small angles for $\phi_{||}$ and ϕ^* and expanding $\sin \alpha$ and $\cos \alpha$, one has

$$\sin \alpha \approx \left(1 - \frac{\phi_{||}^2}{2}\right) \left(-\frac{\phi^*}{2} + \frac{\phi^*}{2} s(t)\right) + \phi_{||} \left[\frac{\phi^{*2}}{4} + \left(1 - \frac{\phi^*}{4}\right) s(t)\right] \quad (\text{C-5})$$

$$\sin^2 \alpha \approx (1 - s(t)) \frac{\phi^{*2}}{4} + \phi_{||} + \frac{\phi_{||}\phi^*}{2} (1 - s(t))$$

$$\cos \alpha \approx \left(1 - \frac{\phi_{||}^2}{2}\right) \left[\frac{\phi^*}{4} + \left(1 - \frac{\phi^{*2}}{4}\right) s(t)\right] + \frac{\phi_{||}\phi^*}{2} (1 - s(t))$$

$$\cos^2 \alpha \approx 1 + \frac{\phi^{*2}}{2} (s(t) - 1) - \frac{\phi_{||}\phi^*}{2} (1 - s(t)) - \phi_{||}^2$$

From (C-3) and (C-5) it follows that

$$V_{xx} = -\frac{eq}{2} (1 - 3\phi_1^2) \quad (\text{C-6})$$

$$V_{yy} = -\frac{eq}{2} \left[1 - \frac{3\phi^{*2}}{2} (1 - s(t)) - 3\phi_{||}^2 + -\frac{\phi_{||}\phi^*}{2} (1 - s(t))\right]$$

$$V_{zz} = -\frac{eq}{2} \left[-2 + 3\phi_1^2 + 3\phi_{||}^2 + \frac{3\phi^{*2}}{2} (1 - s(t)) + \frac{3\phi_{||}\phi^*}{2} (1 - s(t))\right]$$

$$V_{xy} = -\frac{3eq}{2} \phi_1 \left(-\frac{\phi^*}{2} + \frac{\phi^*}{2} s(t) + \phi_{||} s(t)\right)$$

$$V_{xz} = \frac{3eq}{2} \phi_1 \left[\frac{\phi^{*2}}{4} + s(t) \left(1 - \frac{\phi^{*2}}{4}\right) + \frac{\phi_{||}\phi^*}{2} (1 - s(t))\right]$$

$$V_{yz} = -\frac{3eq}{2} \left(-\frac{\phi^*}{2} s(t) + \frac{\phi^*}{2} + \phi_{||}\right)$$

Assuming $\phi_{\perp}$ and ϕ^* are not correlated and also that $\langle \phi_{\parallel} \rangle = 0$, the librational average of (C-6) is given by

$$\langle V_{xx} \rangle = -\frac{eq}{2} (1 - 3 \langle \phi_{\perp}^2 \rangle) \quad (C-7)$$

$$\langle V_{yy} \rangle = -\frac{eq}{2} \left[1 - \frac{3\phi^{*2}}{2} (1 - \langle s(t) \rangle) - 3 \langle \phi_{\parallel}^2 \rangle \right]$$

$$\langle V_{zz} \rangle = -\frac{eq}{2} \left[-2 + 3 \langle \phi_{\perp}^2 \rangle + 3 \langle \phi_{\parallel}^2 \rangle + \frac{3\phi^{*2}}{2} (1 - \langle s(t) \rangle) \right]$$

$$\langle V_{xy} \rangle = \langle V_{xz} \rangle = \langle V_{yz} \rangle = 0$$

The quadrupole Hamiltonian can be divided into two parts

$$H_Q = \langle H_Q \rangle + [H_Q - \langle H_Q \rangle] \quad (C-8)$$

The average Hamiltonian $\langle H_Q \rangle$ gives the NQR frequency, while the second part drives the relaxation process and causes the line to broaden [58].

The fluctuating terms of the components of the EFG tensor can be written as

$$V_{zz} - \langle V_{xx} \rangle = -\frac{3eq}{2} (\phi_{\perp}^2 - \langle \phi_{\perp}^2 \rangle) \quad (C-9)$$

$$V_{yy} - \langle V_{yy} \rangle = \frac{3eq}{2} \left[\phi_{\parallel}^2 - \langle \phi_{\parallel}^2 \rangle - \frac{3\phi^{*2}}{2} (s(t) - \langle s(t) \rangle) - \frac{3\phi_{\parallel}\phi^*}{2} (1 - s(t)) \right]$$

$$V_{zz} - \langle V_{zz} \rangle = -\frac{3eq}{2} [\phi_{\perp}^2 - \langle \phi_{\perp}^2 \rangle + \phi_{\parallel}^2 - \langle \phi_{\parallel}^2 \rangle + \frac{\phi^{*2}}{2} (s(t) - \langle s(t) \rangle) + \frac{3\phi_{\parallel}\phi^*}{2} (1 - s(t))]$$

$$V_{xy} - \langle V_{xy} \rangle = -\frac{3eq}{2} \phi_{\perp} \left[-\frac{\phi^*}{2} (1 - s(t)) + \phi_{\parallel} s(t) \right]$$

$$V_{xz} - \langle V_{xz} \rangle = \frac{3eq}{2} \phi_{\perp} s(t)$$

$$V_{yz} - \langle V_{yz} \rangle = -\frac{3eq}{2} \left[\frac{\phi^*}{2} (1 - s(t)) + \phi_{\parallel} \right]$$

where in (C-9) consideration is given only to the second order of $\phi_{||}$, $\phi_{\perp}$ and ϕ^* .

For spin $I = \frac{5}{2}$, the NQR frequency between $m = \pm\frac{5}{2}$ and $m = \pm\frac{3}{2}$, T_2 is given by [58].

$$\frac{1}{T_2} = \frac{1}{T_2} + \frac{1}{2} \left[\frac{1}{T_{\pm 5/2}} + \frac{1}{T_{\pm 3/2}} \right] \quad (C-10)$$

where

$$\frac{1}{T_2} = \int_0^{\infty} \frac{\omega'(t) \omega'(t-\tau)}{\omega'(t) \omega'(t-\tau)} d\tau$$

$\omega'(t)$ is the departure of the instantaneous resonance frequency from its average value and

$$\frac{1}{T_{\pm 5/2}} = \sum_{m \neq \pm 5/2} w_{\pm 5/2, m} \quad (C-11)$$

$$\frac{1}{T_{\pm 3/2}} = \sum_{m \neq \pm 3/2} w_{\pm 3/2, m} \quad (C-12)$$

where $T_{\pm 5/2}$ and $T_{\pm 3/2}$ are the lifetimes of the states $m = \pm 5/2$ and $m = \pm 3/2$ respectively. From (A-1) and (C-9) one will have, assuming order phase $\langle s(t) \rangle = 0$

$$\begin{aligned} \omega'(t) = & \left[-\frac{9eQq}{20\hbar} \right] \frac{3}{\sqrt{6}} [\phi_{\perp}^2 - \langle \phi_{\perp}^2 \rangle + \phi_{||}^2 - \langle \phi_{||}^2 \rangle] \\ & + \frac{\phi^{*2}}{2} s(t) + \frac{3}{2} \phi_{||} \phi^* s(t) \end{aligned} \quad (C-13)$$

Since $\phi_{||}$ and $\phi_{\perp}$ occur at higher frequencies, for simplicity one may neglect these terms. One would then have

$$\int_0^{\infty} \omega'(t) \omega'(t-\tau) d\tau = \left[\frac{9e^2Qq}{20\hbar} \right]^2 \frac{3 \langle \phi^{*4} \rangle}{8} \int_0^{\infty} s(t) s(t-\tau) d\tau \quad (C-14)$$

Defining

$$\int_{-\infty}^{\infty} \frac{s(t) s(t-\tau)}{s(t) s(t-\tau)} e^{-i\omega\tau} d\tau = J_{II}(\omega) \quad (C-15)$$

it follows from (C-14) and (C-15) that

$$\frac{1}{T_2} = \left[\frac{9e Qq}{20h} \right]^2 \frac{3 < \phi^{*4} >}{16} J_{II}(0) \quad (C-16)$$

Consider now for $\frac{1}{T_{\pm 5/2}}$ terms. From (C-11), one writes

$$\frac{1}{T_{\pm 5/2}} = w_{\pm 5/2, \pm 3/2} + w_{\pm 5/2, \pm 1/2}$$

Using (A-1), (A-4), (A-4'), (A-6) and (A-6') one obtains

$$\begin{aligned} \frac{1}{T_{\pm 5/2}} = & \left[\frac{eQ}{40h} \right]^2 80 \left[\int_{-\infty}^{\infty} \frac{V_{+1}(t) V_{+1}^*(t-\tau)}{V_{+1}(t) V_{+1}^*(t-\tau)} e^{-i\omega\tau} d\tau \right. \\ & + \left. \int_{-\infty}^{\infty} \frac{V_{-1}(t) V_{-1}^*(t-\tau)}{V_{-1}(t) V_{-1}^*(t-\tau)} e^{-i\omega\tau} d\tau \right] \\ & + \left[\frac{eQ}{40h} \right]^2 40 \left[\int_{-\infty}^{\infty} \frac{V_{+2}(t) V_{+2}^*(t-\tau)}{V_{+2}(t) V_{+2}^*(t-\tau)} e^{-i\frac{3}{2}\omega\tau} d\tau \right. \\ & + \left. \int_{-\infty}^{\infty} \frac{V_{-2}(t) V_{-2}^*(t-\tau)}{V_{-2}(t) V_{-2}^*(t-\tau)} e^{-i\frac{3}{2}\omega\tau} d\tau \right] \end{aligned} \quad (C-17)$$

Now one needs to consider

$$A = \int_{-\infty}^{\infty} \frac{V_{\pm 1}(t) V_{\pm 1}^*(t-\tau)}{V_{\pm 1}(t) V_{\pm 1}^*(t-\tau)} e^{-i\omega\tau} d\tau$$

where

$$\begin{aligned} A = & \left[\frac{3eq}{2} \right]^2 \left[\int_{-\infty}^{\infty} \frac{\phi_{\pm}(t) s(t) \phi_{\pm}(t-\tau) s(t-\tau)}{\phi_{\pm}(t) s(t) \phi_{\pm}(t-\tau) s(t-\tau)} e^{-i\omega\tau} d\tau \right. \\ & + \int_{-\infty}^{\infty} \frac{\phi_{\pm 2}^*(t) s(t) s(t-\tau)}{\phi_{\pm 2}^*(t) s(t) s(t-\tau)} e^{-i\omega\tau} d\tau + \int_{-\infty}^{\infty} \frac{\phi_{\pm}(t) \phi_{\pm}(t-\tau)}{\phi_{\pm}(t) \phi_{\pm}(t-\tau)} e^{-i\omega\tau} d\tau \end{aligned} \quad (C-18)$$

and where no correlation between the value of ϕ^* and $s(t)$ has been assumed.

If one assumes an harmonic oscillator for $\phi_{\perp}$ and $\phi_{\parallel}$, and for $s(t)$ an exponential correlation function with characteristic time τ_2'' , it follows from (C-18) that

$$A = \left(\frac{3eq}{2} \right)^2 \left[\frac{\langle \phi_{\perp}^2 \rangle}{1 + (\omega_{\perp} + \omega)^2 \tau_2''^2} + \frac{\langle \phi^*{}^2 \rangle}{4} \frac{1}{1 + \omega^2 \tau_2''^2} \right] \quad (C-19)$$

One notes that $\omega_{\perp} \gg \omega$ and $\omega_{\perp} \tau_2'' \gg 1$.

$$A = \left(\frac{3eq}{2} \right)^2 \left[\frac{\langle \phi_{\perp}^2 \rangle}{\omega_{\perp}^2 \tau_2''^2} + \frac{\langle \phi^*{}^2 \rangle}{4} \frac{1}{1 + \omega^2 \tau_2''^2} \right]$$

(C-20) can be reduced to

$$A = \left(\frac{3eq}{2} \right)^2 \frac{\langle \phi^*{}^2 \rangle}{4} \frac{1}{1 + \omega^2 \tau_2''^2} \quad (C-21)$$

While for

$$B = \int_0^{\infty} \frac{V_{\pm 2}(t) V_{\pm 2}^*(t - \tau)}{\tau} e^{-i\omega \tau} d\tau$$

Since $V_{\pm 2}$ involves $V_{\pm 2}$, one needs only to consider, assuming $\langle s(t) \rangle = 0$,

$$V_{yy} - \langle V_{yy} \rangle \approx - \frac{3eq}{2} \left[\frac{3\phi^*{}^2}{2} s(t) - \frac{3\phi_{\parallel}\phi^*}{2} (1 - s(t)) \right] \quad (C-22)$$

and

$$V_{xy} - \langle V_{xy} \rangle \approx - \frac{3eq}{2} \left[- \frac{\phi_{\perp}\phi^*}{2} (1 - s(t)) + \phi_{\perp}\phi_{\parallel} s(t) \right]$$

If one further assumes that no correlation exists between $\phi_{\parallel}$, $\phi_{\perp}$, ϕ^* and $s(t)$, (C-22) can be simplified as

$$V_{yy} - \langle V_{yy} \rangle \approx - \frac{3eq}{2} \frac{3\phi^*{}^2}{2} s(t) \quad (C-22')$$

$$V_{xy} - \langle V_{xy} \rangle \approx 0$$

It follows that

$$B = \left(\frac{3eq}{2} \right)^2 \frac{9 \langle \phi^{*4} \rangle}{4} \int_{-\infty}^{\infty} \frac{s(t) \overline{s(t-\tau)} e^{-i\frac{3}{2}\omega\tau}}{s(t) \overline{s(t-\tau)}} e^{-i\frac{3}{2}\omega\tau} d\tau \quad (C-23)$$

$$= \left(\frac{3eq}{2} \right)^2 \frac{9 \langle \phi^{*4} \rangle}{4} J_{II} \left(\frac{3}{2} \omega \right)$$

From (C-17), (C-21) and (C-23)

$$\frac{1}{T_{\pm 5/2}} = \left[\frac{3e^2 Q q}{80\hbar} \right]^2 \left[80 \langle \phi^{*2} \rangle \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} + 180 \langle \phi^{*4} \rangle J_{II} \left(\frac{3}{2} \omega \right) \right] \quad (C-24)$$

Considering now the $\frac{1}{T_{\pm 3/2}}$ term and using (A-1), (A-4), (A-4'), (A-5), (A-5'), (A-6) and (A-6'), one writes

$$\begin{aligned} \frac{1}{T_{\pm 3/2}} = & \left(\frac{eQ}{40\hbar} \right)^2 80 \left[\int_{-\infty}^{\infty} \overline{V_{+1}(t)} V_{+1}^*(t-\tau) e^{-i\omega\tau} d\tau \right. \\ & + \left. \int_{-\infty}^{\infty} \overline{V_{-1}(t)} V_{-1}^*(t-\tau) e^{-i\omega\tau} d\tau \right] \\ & + \left(\frac{eQ}{40\hbar} \right)^2 32 \left[\int_{-\infty}^{\infty} \overline{V_{+1}(t)} V_{+1}^*(t-\tau) e^{-i\frac{\omega}{2}\tau} d\tau \right. \\ & + \left. \int_{-\infty}^{\infty} \overline{V_{-1}(t)} V_{-1}^*(t-\tau) e^{-i\frac{\omega}{2}\tau} d\tau \right] \\ & + \left(\frac{eQ}{40\hbar} \right)^2 72 \left[\int_{-\infty}^{\infty} \overline{V_{+2}(t)} V_{+2}^*(t-\tau) e^{-i\frac{\omega}{2}\tau} d\tau \right. \\ & + \left. \int_{-\infty}^{\infty} \overline{V_{-2}(t)} V_{-2}^*(t-\tau) e^{-i\frac{\omega}{2}\tau} d\tau \right] \end{aligned} \quad (C-25)$$

Employing the A and B terms as discussed above, one writes

$$\begin{aligned} \frac{1}{T_{\pm 3/2}} = & \left[\frac{9e^2 Q q}{20\hbar} \right]^2 \left[\frac{5}{9} \langle \phi^{*2} \rangle \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} \right. \\ & + \left. \frac{2}{9} \langle \phi^{*2} \rangle \frac{\tau_2'^2}{1 + \frac{1}{4} \omega^2 \tau_2'^2} + \frac{9}{4} \langle \phi^{*4} \rangle J_{II} \left(\frac{1}{2} \omega \right) \right] \end{aligned} \quad (C-25)$$

From (C-10), (C-24) and (C-26), one has

$$\begin{aligned} \frac{1}{T_2} = & \left[\frac{9e^2Qq}{20\hbar} \right]^2 \left[\frac{3}{16} \langle \phi^{*4} \rangle J_{II}(0) + \frac{9}{4} \langle \phi^{*4} \rangle J_{II}\left(\frac{1}{2}\omega\right) \right. \\ & + \frac{5}{4} \langle \phi^{*4} \rangle J_{II}\left(\frac{3}{2}\omega\right) + \frac{10}{9} \langle \phi^{*2} \rangle \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} \\ & \left. + \frac{2}{9} \langle \phi^{*2} \rangle \frac{\tau_2'^2}{1 + \frac{1}{4}\omega^2 \tau_2'^2} \right] \end{aligned} \quad (C-27)$$

If one assumes fast motion, i.e. $J_{II}(0) \approx J_{II}\left(\frac{1}{2}\omega\right) \approx J_{II}(\omega) \approx J_{II}\left(\frac{3}{2}\omega\right)$, one can neglect terms involving $\langle \phi^{*4} \rangle$ since ϕ^* is a small angle. One then has

$$\frac{1}{T_2} = \left[\frac{9e^2Qq}{20\hbar} \right]^2 \langle \phi^{*2} \rangle \left[\frac{10}{9} \frac{\tau_2'^2}{1 + \omega^2 \tau_2'^2} + \frac{2}{9} \frac{\tau_2'^2}{1 + \frac{1}{4}\omega^2 \tau_2'^2} \right] \quad (C-28)$$

These terms on the right hand side of (C-28) came from the lifetime of the states $m = \pm \frac{5}{2}$ and $m = \pm \frac{3}{2}$, while the adiabatic term $\frac{1}{T_2}$ has been neglected. One can also show that for

$$\tau_2' \approx 1.188 \frac{1}{\omega} \quad (C-29)$$

(C-28) has a maximum.

One thing worth noting in (C-7) is that $\langle V_{zz} \rangle$ shows the usual Bayer-type dependence for the NQR resonance frequency even though it is derived from the small angle ϕ^* . One also notes that for large ϕ^* , i.e. significantly different from π reorientation, $\langle V_{zz} \rangle$ will be affected.

In the fast motion regime, $\omega\tau_2' \ll 1$, (C-28) can be further reduced to

$$\frac{1}{T_2} = \frac{4}{3} \left[\frac{9e^2Qq}{20\hbar} \right]^2 \langle \phi^{*2} \rangle \tau_2' \quad (C-30)$$

which relates the linewidth and the correlation time of the molecular reorientational motion.

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BIOGRAPHICAL SKETCH

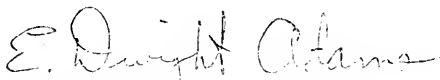
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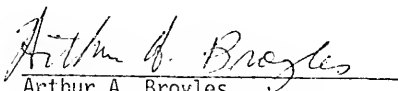
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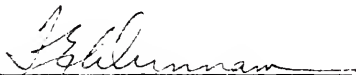
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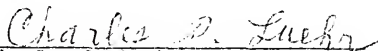
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